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The effect of cooling rates on hereditary characteristics of icosahedral clusters in rapid solidification of liquid $Cu_{56}Zr_{44}$ alloys

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ABSTRACT

A molecular dynamics simulation is performed to investigate the influence of cooling rates γ on the hereditary characteristics of icosahedral clusters during the rapid solidification of liquid $Cu_{56}Zr_{44}$ alloys. The analysis from an extended cluster-type index method based on the H–A bond-type index shows (12 0 12 0 0 0 0 0 0 0) standard icosahedra and (12 0 8 0 0 0 2 2 0 0) as well as (12 2 8 2 0 0 0 0 0 0) defective icosahedra play a key role in the formation of $Cu_{56}Zr_{44}$ glassy alloys. With the increase of cooling rates γ, the glass transformation temperature T_g rises, but the clustering degree towards icosahedra descends in the rapidly solidified solid. An inverse tracking of atom traces reveals the icosahedral clusters at 300 K mainly originate from the configuration heredity below T_g, and the perfect heredity is dominant among perfect, core and segmental heredity modes. Relative to (12 0 8 0 0 0 2 2 0 0) and (12 2 8 2 0 0 0 0 0 0) defective icosahedra, (12 0 12 0 0 0 0 0 0 0) standard icosahedra are of high structural stability and large heredity ability, and their descendible efficiencies and heredity behaviors vary with γ. In the case of high γ, not only the descendible fractions f_i of icosahedral clusters above T_g are enlarged, but also their initial descendible temperatures T_{onset} in the super-cooled liquid region are elevated. As a result, icosahedral medium-range orders (IMROs) can be easily formed and grown in the super-cooled liquid. Therefore, a big $T_{rg} = T_g/T_m$ of $Cu_{56}Zr_{44}$ alloys at high γ can be attributed to the ascent of T_{onset} caused by increasing γ to some extent.

1. Introduction

Metallic glasses (MGs) have attracted extensive attention owing to their scientific and engineering significances [1–5]. In the past decades, a great deal of efforts [4–8] was devoted to developing an appropriate parameter to assess the glass forming ability (GFA) of various alloy systems. Based on experiments and theoretical analysis, several criteria have been proposed, such as the three principles of Inoue [4], the confusion rule of Johnson [5] and the fragility parameter of Angell [6,7]. But they fail to provide an insight into the structural origin of the formation of glassy alloys [3]. Recently, many researchers have recognized that the GFA is intimately correlated with the microstructure of alloy melts [9–19], especially the local geometry and chemical composition of icosahedral clusters [9–12,15–19]. As a major structural unit in liquid alloys and metallic glasses, icosahedra have been demonstrated to play a key role in the formation of TM–TM amorphous alloys [1,19]. Since metallic glasses are called 'frozen liquids', a strong hereditable ability of icosahedra in metal melts undoubtedly means that the rapidly solidified alloy is of a high GFA. Hence, the GFA of TM–TM systems can be evaluated by the number and configuration of icosahedral clusters inherited from metal melts to some extent [20]. It is well known, the evolution of microstructure strongly depends on cooled conditions and melted histories in the rapid solidification process of liquid alloys. Lots of experiments [1,11,21] and molecular dynamics (MD) simulations [22–24] have shown that not only the preference of the nucleation of icosahedral quasicrystal and Laves phases can be strongly affected by a preexisting local order in the liquid [11], but the configuration and feature of icosahedral clusters in glassy alloys can also be changed by cooling rates γ and imposed pressures P [10,21–24]. To understand the correlation of GFA with heredity of icosahedral clusters, a detailed investigation on the evolution of icosahedral clusters at various γ is desired.

The Cu–Zr alloy system is a representative of TM–TM metallic glasses with a good GFA over a wide range of compositions [12–15,25–27]. Previous investigations indicate the packing density of glassy alloys is closely correlated with the GFA of Cu–Zr alloys [27], and some short-range orders (SROs) [9–12] even medium-range orders (MROs) [9,12,28,29] can be detected in densely packed Cu–Zr metallic glasses. The Cu-centered icosahedra have been utilized to characterize the glassy transition [15,20] even evaluate the GFA as a fundamental structural feature [15], and the composition with the best GFA may be described by the "cluster + glue atoms" scheme, *e.g.*, $Cu_{56}Zr_{44} = Cu_7Zr_6 + Cu$ [30]. Our recent investigation [20] further reveals the configuration heredity of icosahedral clusters in the super-cooled liquid is an intrinsic feature of rapidly solidified $Cu_{50}Zr_{50}$ alloys. The onset state merely emerges in the super-cooled liquid rather than the initial equilibrium liquid during the

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rapid solidification of liquid $Cu_{50}Zr_{50}$ alloys. As a subsequent step towards an in-depth understanding of the evolution of microstructures in the formation of glassy alloys, a cooling rate γ dependent heredity of icosahedral clusters in liquid $Cu_{56}Zr_{44}$ alloys will be investigated in this work, and special attention will be paid on the correlation between the heredity-induced clustering towards icosahedra and the GFA of Cu–Zr alloys.

2. Simulation method

Using a large-scale atomic/molecular massively parallel simulator (LAMMPS) code [31], several MD simulations of the rapid solidification process of liquid $Cu_{56}Zr_{44}$ alloys were carried out, in which 10,000 atoms (5600 Cu atoms and 4400 Zr atoms) in a cubic box subjected to the periodic boundary condition were considered, and their motion equations were solved by Verlet's algorithm in the velocity form with a time step of 1 fs. Constant pressure *P* and temperature *T* were imposed by the modified Nose–Hoover method [32] for both *P* and *T* variables and an embedded-atom model (EAM) potential developed recently for the Cu–Zr alloys [33] in a many-body framework was utilized. The $Cu_{56}Zr_{44}$ alloy was initially melted and equilibrated for 1 ns at 1600 K well above the experimental melting temperature $T_m = 1191$ K [13], and subsequently the liquid was cooled down to 300 K at five different cooling rates ($\gamma_1 = 10$ K/ns, $\gamma_2 = 10^2$ K/ns, $\gamma_3 = 10^3$ K/ns, $\gamma_4 = 10^4$ K/ns and $\gamma_5 = 10^5$ K/ns). The cooling run was performed in the *NPT* ensemble with zero pressure. In our simulation, a primary temperature interval and the isothermal running time at selected temperatures were set as 100 K and 0.1 ps, respectively. Moreover, a temperature interval of 10 K was also adopted to obtain exact information of atomic positions at some special stages of solidification, *e.g.*, the temperatures near by the glass transition.

3. Result and discussion

3.1. Reduced glass transition temperature T_{rg}

Fig. 1 plots total radial distribution functions $g_{total}(r)$ of initial liquid and final solid at different γ. One can see that the first peak of g(*r*) curves in rapidly solidified solid becomes sharp and the second peak of g(*r*) curves exhibits a distinct shoulder relative to liquid, which means numerous SROs even some MROs emerge in rapidly solidified solids at 300 K [11,18], and the rapidly solidified solids are of amorphous characteristics [14]. The split second peak and an increasing shoulder in the g(*r*) curves further indicate the number of icosahedron-like MROs rises with the decrease of γ at 300 K [12]. As temperature *T* dependent total energies *E* per atom are being considered (refer to the insert in Fig. 2), it is found no abrupt change in *E* can be observed, which means the first order phase transitions such as the crystallization [18] are absent in the present simulated system. By means of extrapolating and intersecting two linear parts of *E vs T* curve from 300 K to 1400 K, the glass transition temperature T_g of $Cu_{56}Zr_{44}$ alloys is also deduced. For $\gamma_1 = 10$ K/ns, $\gamma_2 = 10^2$ K/ns, $\gamma_3 = 10^3$ K/ns, $\gamma_4 = 10^4$ K/ns and $\gamma_5 = 10^5$ K/ns, the evaluated T_g values are 912 K, 926 K, 943 K, 958 K and 972 K, respectively. Correspondingly, their reduced glass transition temperatures $T_{rg} = T_g/T_m$ are determined to be 0.766, 0.777, 0.792, 0.804 and 0.816, respectively, as shown in Fig. 2. Present T_g values are higher than the experimental value of 674 K [13], but very close to the previously simulated result of 940 K [34]. Similarly to the result in Ref. [14], the T_{rg} varies linearly with lgγ and ascends with increasing γ, which means a high γ is in favor of the glass transition of $Cu_{56}Zr_{44}$ alloys.

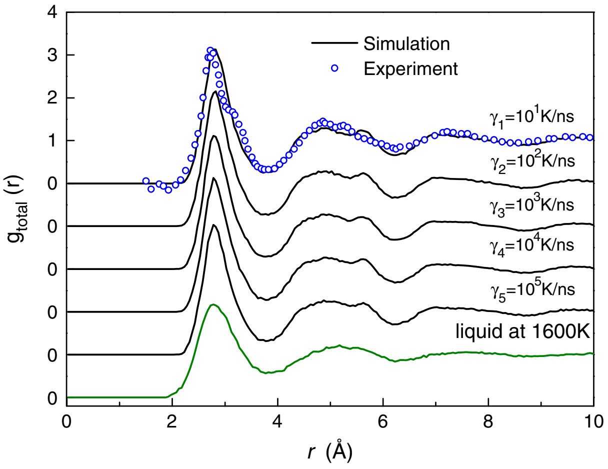

Fig. 1. The total g(*r*) curves of $Cu_{56}Zr_{44}$ alloys at 300 K and 1600 K. The experimental data are taken from literature [26].

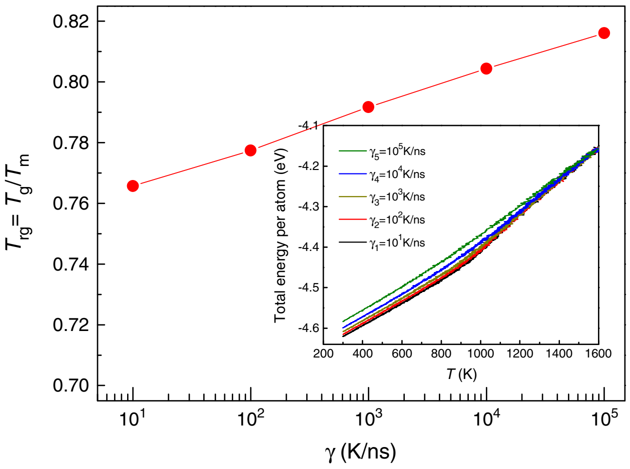

Fig. 2. The cooling rate γ dependence of deduced glass transition temperatures $T_{rg} = T_g/T_m$. The insert is the total energy per atom as a function of temperature *T* in $Cu_{56}Zr_{44}$ alloy system.

3.2. Identification of icosahedral clusters

The Honeycutt–Andersen (H–A) bond-type index method [35] is adopted to characterize microstructures of $Cu_{56}Zr_{44}$ alloys during the rapid solidification. In this pair analysis technique, two atoms are regarded to be near-neighbors and form a bond if they are within a specified cutoff distance. Herein the cutoff distance corresponds to the first minimum r_{min} in partial radial distribution function $g_{\alpha\beta}(r)$ curves. A sequence of four integers (*ijkl*) is designed to describe the different local configurations. The first integer *i* is a remark of the bonding between two given atoms. *i* is 1 when the atoms in the root pair are bonded, otherwise *i* is 2. The second integer *j* is the number of near-neighbor atoms shared in common by the root pair. The third integer *k* is the number of bonds among the shared neighbors. The fourth integer *l* is needed to distinguish configurations with the same first three indices but different bonding geometries. This method has been proved to be successful in assessing local configurations of liquid and amorphous alloys [19,36]. For example, 1551 bond-pair represents two root pair atoms with five common neighbors, among which five bonds form a pentagon by near-neighbor contact, as shown in Fig. 3. In this case, some typical bonded pairs are examined to understand the local structures of simulated system. For example, the number of 1551 bond-pairs with five-fold symmetry is a measure of the degree of ideal icosahedral short-range order. 1421 and 1422 bond-pairs are characteristic bond-pairs of fcc and hcp crystal structures, respectively. 1661 and 1441 bond-pairs are characteristic bond-pairs of bcc crystal structure [37].

As an example, Table 1 lists the variation of various H–A bond-types with *T* in $Cu_{56}Zr_{44}$ alloy system at $\gamma_1 = 10$ K/ns. It is noticed that 1551,