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# Glass forming abilities of binary $Cu_{100-x}Zr_x$ (34, 35.5, and 38.2 at. %) metallic glasses: A LAMMPS study

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Using large-scale atomic/molecular massively parallel simulator (LAMMPS), we have studied the liquid behaviors of $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$ amorphous alloys including their pair distribution functions, distributions of Voronoi clusters with different coordination numbers, and mean square displacements of Cu and Zr atoms. Compared to $Cu_{61.8}Zr_{38.2}$ and $Cu_{66}Zr_{34}$, we found high concentrations of distorted icosahedra with indices of $\langle 0,2,8,2\rangle$ and $\langle 0,4,4,4\rangle$, high numbers of Cu-centered $Cu_8Zr_5$ and $Cu_9Zr_4$ clusters, and reduced atomic diffusivity of Cu and Zr atoms in molten $Cu_{64.5}Zr_{35.5}$ alloy. These effects would benefit glass formation in $Cu_{64.5}Zr_{35.5}$ alloy. Meanwhile, from the viewpoints of local cluster structure, the majority of the glue atoms are Cu atoms in $Cu_{64.5}Zr_{35.5}$ amorphous alloy, which leads to denser packing and better glass forming ability. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3081979]

## I. INTRODUCTION

Since the first discovery of a metallic glass (MG) in the early 1990s, bulk metallic glasses (BMGs) have been extensively studied because certain mechanical properties, such as strength, can be significantly improved over their crystalline counterparts.[1–4] Recent studies on the BMGs show that proper estimation of glass forming ability (GFA) is important for developing new BMG materials with improved properties and for engineering applications. Based on experimental results, a variety of schemes have been proposed to evaluate GFA,[5] such as the negative heat of formation, a large difference in atomic sizes of constituents, and a low liquidus eutectic. However, due to the lack of understanding of the local atomic structure of BMGs,[6] the design of alloys with a high GFA remains unpredictable to a large extent.

Furthermore, correlations between parameters describing atomic structure of BMGs and their properties, such as correlation between volumetric change and GFA,[7] and correlation between fragility and GFA/plasticity,[8] have been the focus of many studies since atomic structure determines the properties of materials. Unfortunately, in the case of Cu–Zr alloy, there exist discrepancies between the monotonic behaviors of structural parameters, such as atomic packing density[9] and atomic pair distribution functions (PDFs),[10] and the nonlinear variation in the GFAs of amorphous $Cu_{100-x}Zr_x$ alloys.[11] Despite many studies,[12–15] this remains an unsolved puzzle so far.

To clarify this issue on a more quantitative level, in this work, we investigate local atomic structures and thermophysical properties of binary $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$ MGs in molten states and relate them to the GFAs of these alloys. Based on the fact that most MGs are made from melts by quenching techniques,[16,17] it is useful to investigate the molten structure of binary alloys. Computer simulation using the large-scale atomic/molecular massively parallel simulator (LAMMPS) method is able to provide detailed atomic structural information which experiments have limited access. In this letter, we report calculated PDFs $g(r)$, distributions of Voronoi clusters (VCs) with different coordination numbers (CNs), and mean square displacements (MSDs) of Cu and Zr atoms in $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$ melts. In addition, we also elucidated the GFAs of binary $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$ MGs from the viewpoints of their local cluster structure.

## II. THEORETICAL METHODS

We have performed molecular dynamics (MD) simulation based on the embedded atom method potential in the *NPT* (constant number of particles-pressure-temperature) ensemble by using the LAMMPS code,[10,18] which is a highly scalable classical MD code designed for simulating molecular and atomic systems on parallel supercomputers. The MD simulations were carried out using a super cell containing 16 000 atoms under periodic boundary conditions. To simulate a random alloy with a given composition, we randomly substituted appropriate amount of copper (zirconium) atoms with the same number of zirconium (copper) atoms in the initial *B*2 structure ($Cu_{50}Zr_{50}$). The *NPT* MD simulations were performed in steps of 100 K, in a temperature range from 0 to 2400 K. The temperature is high up to 2400 K in order to allow atoms to diffuse and "forget" their initial positions. A time step of 1 fs was used. At each temperature the MD simulation time for determining the properties was 20 ps. The simulated melting temperature is higher than that observed in experiment due to the homogeneous model system without a free surface and the high heating rate.[18]

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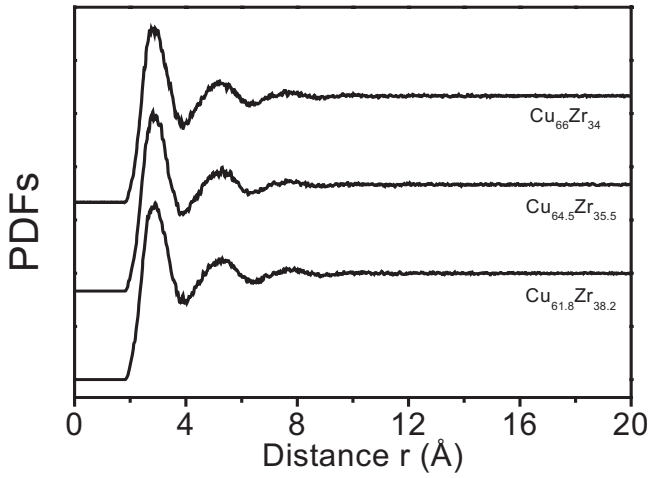


FIG. 1. PDFs $g(r)$ for $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$ molten alloys, respectively.

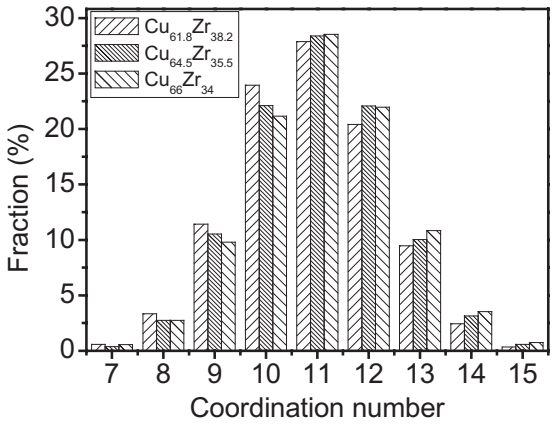


FIG. 2. Total fractions of VCs with different CNs for the $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$ molten alloys deduced by Voronoi tessellation method.

## III. RESULTS AND DISCUSSION

For a molten multicomponent alloy, the PDF $g(r)$ is an effective method to describe its structure. The total $g(r)$ can be calculated as

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

where $N$ denotes the number of atoms in the simulation cell, $V$ is the volume of the same cell, and $n(r)$ is the number of particles which can be found in the shell from $r$ to $r+\Delta r$. The calculated total PDFs of molten $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$ are illustrated in Fig. 1. No splitting of the second peaks is observed. Also the shell numbers of these three alloys are almost the same.

To further examine the differences in the local structures, we employ the Voronoi tessellation method by setting a cutoff distance of 3.6 Å.[19,20] VCs are defined as closed polyhedra with one center atom, piled up with tetrahedra. Various VCs can be indexed as $\langle n_3, n_4, n_5, n_6, \ldots \rangle$, where $n_i$ is the number of shell atoms which are connected with other $i$th shell atoms.[20] The total fractions of various VCs centered at Cu and Zr atoms with different CNs in the $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$ molten alloys are shown in Fig. 2. It is clear that VCs with CN=11 are dominant in all three molten alloys. In addition, $Cu_{61.8}Zr_{38.2}$ contains slightly more VCs with CN=9 and 10 but less VCs with CN=12 and 13, compared to $Cu_{64.5}Zr_{35.5}$ and $Cu_{66}Zr_{34}$. Similarly, $Cu_{66}Zr_{34}$ contains slightly more VCs with CN=13 and 14 but less VCs with CN=9 and 10 than $Cu_{61.8}Zr_{38.2}$ and $Cu_{64.5}Zr_{35.5}$. More importantly, $Cu_{64.5}Zr_{35.5}$, the best glass former among the three alloys being considered, has the highest concentration of VCs with CN=12. Most of the VCs with CN=12 are in the form of distorted icosahedra with indices of $\langle 0,3,6,3 \rangle$, $\langle 0,2,8,2 \rangle$, and $\langle 0,4,4,4 \rangle$, and concentrations of $\langle 0,2,8,2 \rangle$ and $\langle 0,4,4,4 \rangle$ are relatively higher in molten $Cu_{64.5}Zr_{35.5}$, as shown in Table I. In addition, it is worth noting that the Cu-centered VCs with indices of $\langle 0,2,8,2 \rangle$ and $\langle 0,4,4,4 \rangle$ have the same tendency mentioned above, indicating that the Cu-centered distorted icosahedra mainly contribute to this phenomenon.

We further compared the local cluster structure of molten $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$. For Cu-centered clusters with CN=12, the majority clusters are $Cu_8Zr_5$ and $Cu_9Zr_4$. Compared to $Cu_{61.8}Zr_{38.2}$ and $Cu_{66}Zr_{34}$, high numbers of Cu-centered $Cu_8Zr_5$ and $Cu_9Zr_4$ clusters are observed in molten $Cu_{64.5}Zr_{35.5}$ alloy, as shown in Table I.

The viscosity of a molten liquid is related to the diffusivity of the liquid atoms and, therefore, to the GFA of the alloy. The viscosity of a liquid is given by the Stokes–Einstein equation

$$\eta = \frac{k_B T}{3\pi\lambda D}, \tag{2}$$

where $\lambda$ is a jump distance on the order of atomic dimensions and $D$ is the diffusion coefficient. Moreover, the viscosity of a molten liquid is associated with the liquid fragility. Therefore, the viscosity in the molten liquid state is an important kinetic parameter, which may influence the GFA of the alloy as well as its fragility. Hence, atom displacements of different chemical species should be studied as a function of time in order to simulate diffusion and the value of the MD time window becomes a critical parameter in estimating values of diffusion coefficients. For this reason, the MSDs of Cu and Zr atoms are obtained at temperatures in the liquid phase as they can provide qualitative information on how the different chemical species evolve with time and with different chemical environments. This is shown in Fig. 3 for $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$ at $T=2400$ K with a time step of 3 fs. The MSD is defined as

$$\langle r^2(t) \rangle = \frac{1}{N}\sum_{i=1}^{N} \langle |r_i(t) - r_i(0)|^2 \rangle, \tag{3}$$

where $r_i(t)$ is the atomic position of atom $i$ at time $t$ and $\langle \cdot \rangle$ represents the thermal average. As expected, the MSDs of both Cu and Zr atoms in all molten alloys increase linearly with time. However, the MSDs of Cu and Zr atoms in $Cu_{64.5}Zr_{35.5}$ molten alloy have a smaller rate of increase,

TABLE I. The fractions of the VCs with indices of ⟨0,2,8,2⟩ and ⟨0,4,4,4⟩, respectively, the fractions of the Cu-centered VCs with indices of ⟨0,2,8,2⟩ and ⟨0,4,4,4⟩, respectively, the numbers of the Cu-centered $Cu_8Zr_5$ and $Cu_9Zr_4$ clusters, respectively, and the diffusion coefficients of Cu and Zr atoms for $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$ molten alloys, respectively.

| Alloy compositions | The fractions of ⟨0,2,8,2⟩ and ⟨0,4,4,4⟩ VCs (%) | The fractions of the Cu-centered ⟨0,2,8,2⟩ and ⟨0,4,4,4⟩ VCs (%) | The numbers of Cu-centered $Cu_8Zr_5$ and $Cu_9Zr_4$ clusters | The diffusion coefficients of Cu/Zr atoms ($Å^2$/fs) |
|---|---|---|---|---|
| $Cu_{61.8}Zr_{38.2}$ | 3.90/2.37 | 3.12/2.20 | 440/386 | $3.12\times10^{-3}/2.24\times10^{-3}$ |
| $Cu_{64.5}Zr_{35.5}$ | 4.31/2.60 | 3.52/2.37 | 492/546 | $3.08\times10^{-3}/2.20\times10^{-3}$ |
| $Cu_{66}Zr_{34}$ | 4.08/2.48 | 3.39/2.13 | 460/530 | $3.20\times10^{-3}/2.28\times10^{-3}$ |

compared with those in $Cu_{61.5}Zr_{38.5}$ and $Cu_{66}Zr_{34}$ molten alloys, implying that atomic diffusion in the $Cu_{64.5}Zr_{35.5}$ molten alloy is slower. The reduced atomic diffusivity in $Cu_{64.5}Zr_{35.5}$ liquid would retard its local atomic rearrangements and crystal nucleation rate, and thus benefits its glass formation. To show the effect on atomic diffusivity more clearly, we derived the diffusion coefficients ($D$) of Cu and Zr atoms in $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$ molten alloys from the slope of MSD-time curves, and the results are shows in Table I. The reduced diffusive motion of Cu and Zr atoms is observed in $Cu_{64.5}Zr_{35.5}$ molten alloy. From the above results of the local cluster structures analyzed by Voronoi tessellation method, the lower atomic mobility in $Cu_{64.5}Zr_{35.5}$ molten alloy could be due to the high concentrations of VCs with indices of ⟨0,2,8,2⟩ and ⟨0,4,4,4⟩ and high numbers of Cu-centered $Cu_8Zr_5$ and $Cu_9Zr_4$ clusters. These effects would benefit glass formation in $Cu_{64.5}Zr_{35.5}$ alloy.

From the perspective of local structures, it has been accepted that the microstructure of CuZr MG contains small sized clusters basically of icosahedral-like order.[21,22] Yang *et al.*[5] demonstrated the existence of icosahedron-like clusters ($Cu_8Zr_5$ centered by Cu atoms) in the $Cu_{61.8}Zr_{38.2}$, $Cu_{64}Zr_{36}$, and $Cu_{64.5}Zr_{35.5}$ amorphous alloys. In addition, Xia *et al.*[14] suggested that the best binary glass forming composition $Cu_{64}Zr_{36}$ is composed of the icosahedral $Cu_8Zr_5$ cluster plus Cu glue atoms, and the alloy composition becomes $Cu_8Zr_5+Cu=Cu_{64.3}Zr_{35.7}$. Similarly, minor alloying of the $Cu_8Zr_5$ icosahedral cluster composition by Nb, Sn, Mo, and Ag significantly improved the GFAs and a series of new ternary BMGs was obtained. Alloying by third elements of this $Cu_8Zr_5$ cluster showed that the ternary optimum BMG compositions could be described as "$Cu_8Zr_5$+glue atom cluster." However, there is an error in the optimum composition due to the assumption that the glue atoms are entirely one type of atom. In reality the glue atoms could be a mixture of Cu and Zr atoms. However Cu atoms should be dominant among the glue atoms for the alloys with good GFAs because the fact that Cu atoms have a smaller atomic radius than Zr atoms causes the denser packing and better GFA accordingly. This is the reason why $Cu_{64.5}Zr_{35.5}$ has a better GFA than $Cu_{61.8}Zr_{38.2}$ and $Cu_{66}Zr_{34}$ alloys.

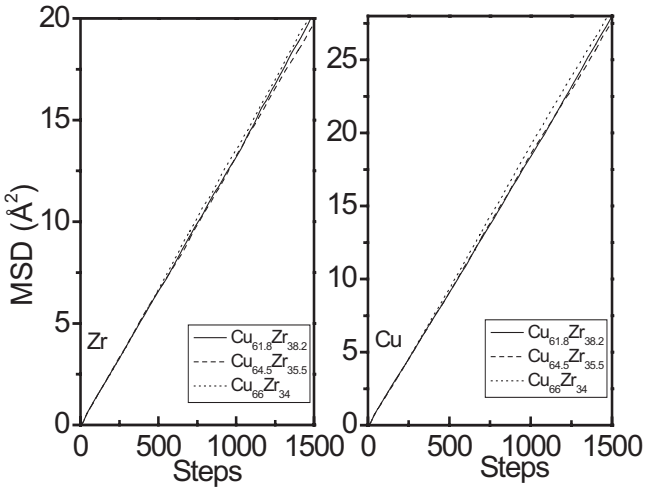


FIG. 3. MSDs of (a) Zr and (b) Cu atoms in $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$ melts, respectively.

## IV. CONCLUSION

In conclusion, we have investigated the correlations between the liquid behaviors of $Cu_{61.8}Zr_{38.2}$, $Cu_{64.5}Zr_{35.5}$, and $Cu_{66}Zr_{34}$ amorphous alloys and their GFAs based on the LAMMPS simulation. In $Cu_{64.5}Zr_{35.5}$ alloy, we observed higher concentrations of VCs with indices of ⟨0,2,8,2⟩ and ⟨0,4,4,4⟩, high numbers of Cu-centered $Cu_8Zr_5$ and $Cu_9Zr_4$ clusters, and reduced atomic diffusivity in liquid. These make the liquid more viscous and thus enhance the GFA. Meanwhile, from the viewpoints of local clusters structure, the majority of the glue atom is Cu in $Cu_{64.5}Zr_{35.5}$ amorphous alloy, which causes denser packing of system and better GFA accordingly.

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