Atomic structure of binary $\text{Cu}_{64.5}\text{Zr}_{35.5}$ bulk metallic glass

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Atomic structures of bulk glass-forming $\text{Cu}_{64.5}\text{Zr}_{35.5}$ and the eutectic composition $\text{Cu}_{61.8}\text{Zr}_{38.2}$ metallic glasses (MGs) have been studied by a combination of state-of-the-art experimental techniques and computational methods. Three-dimensional atomic configuration of the $\text{Cu}_{64.5}\text{Zr}_{35.5}$ MG is established. It is found that icosahedronlike clusters are dominant in both MGs. However, icosahedronlike clusters centered by Cu atoms are slightly denser packing and less distorted in $\text{Cu}_{64.5}\text{Zr}_{35.5}$, which can enhance the glass forming ability (GFA) by suppressing atomic movements and increasing the structural incompatibility with competing crystalline phases. The atomic arrangements from short to medium-range order are envisaged and compared between both MGs.

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With progress in strategies for alloying design, over 20 mm in diameter bulk metallic glasses (BMGs) are achieved in six alloy systems, i.e., Pd-,¹ Zr-,² Y-,³ Mg-,⁴ La-,⁵ and Zr-Cu-based BMGs.⁶ However, the understanding of the atomic structure of BMGs far lags behind,^{7–15} which is mainly caused by the complexity of multicomponent BMGs. The structure of metallic glasses (MGs) was originally described by the model of dense random packing of hard spheres,⁷ in which the glass was pictured as a random arrangement of spherical atoms (hard spheres) with comparative atomic sizes. However, it was also pointed out that the localized, directional chemical bonding, and the formation of groups of atoms are relevant factors to theories of glass formation and stability.⁹ Recently, a topological model for metallic glass formation was proposed.^{13,14} According to that model, a solute occupying either substitutional or interstitial sites in the host lattice can destabilize the lattice by producing a critical internal strain. Particular types of clusters (such as Kasper polyhedra) were suggested to be the main atomic structural units for metallic glasses, by which medium-range order in metallic glasses were illustrated by packing quasiequivalent clusters.¹⁵

BMGs produced usually contain three or more elements. However, simpler systems should be of great interest, fundamentally as well as technologically, since they would facilitate the determination of atomic structure for a given BMG. Recently, binary Cu–Zr BMGs have been synthesized.¹⁶ It was found that the glass forming ability in the system strongly depends on compositions, even narrow down to 1 at. %. Thus, to determine the atomic structure of binary Cu–Zr BMG becomes very important. In this letter, atomic structures of $\text{Cu}_{64.5}\text{Zr}_{35.5}$ BMG, together with eutectic com-

position $\text{Cu}_{61.8}\text{Zr}_{38.2}$ MG ribbon for a comparison, are investigated by a combination of experimental techniques [synchrotron radiation-based x-ray diffraction (XRD) and extended x-ray absorption fine structure (EXAFS)] with computational methods [reverse Monte Carlo (RMC) and *ab initio* molecular dynamics (VASP) simulation]. Three-dimensional (3D) atomic configuration of the $\text{Cu}_{64.5}\text{Zr}_{35.5}$ BMG is established. The atomic arrangements from short to medium range order are envisaged and compared between both glasses.

For $\text{Cu}_{64.5}\text{Zr}_{35.5}$ MG, both 1 mm rod and ribbon were prepared by copper mold injection and single roller melt-spinning technique, respectively, whereas only ribbon sample for $\text{Cu}_{61.8}\text{Zr}_{38.2}$ could be prepared. The high energy XRD was measured on the Petra 2 station with energy of 120 keV ($\lambda = 0.103\,32\,\text{\AA}$) at HASYLAB/DESY, Hamburg. EXAFS spectra at Cu and Zr *K* edge were collected in transmission mode at the beam line X1 of HASYLAB. Standard data analysis was carried out by the same software packages used in Ref. 17. As a completely independent method, the *ab initio* molecular dynamics simulation (VASP) was pursued to simulate 3D atomic structures of these two MGs from a purely theoretical way. By randomly substituting atoms in B2 structure, two clusters with 128 atoms, one is 79 Cu and 49 Zr atoms (marked as $\text{Cu}_{79}\text{Zr}_{49}$) and the other 82 Cu and 46 Zr atoms (marked as $\text{Cu}_{82}\text{Zr}_{46}$), were set up corresponding to compositions $\text{Cu}_{61.7}\text{Zr}_{38.3}$ and $\text{Cu}_{64.1}\text{Zr}_{35.9}$, respectively. In order to save computation time, the LAMMPS package with Rosato-Guillopie-Legrand (RGL)-type many-body potential was initially used during melting and cooling Cu–Zr alloys to obtain amorphous phase. The parameters in RGL-potential and calculation procedure are similar to the work for $\text{Cu}_{46}\text{Zr}_{54}$ MG.¹⁸ After convergence, the atomic configuration was further optimized by VASP-MD using $1 \times 1 \times 1$ *K*-point mesh and projector augmented-wave method (PAW/PBE) standard potentials.¹⁹

Figure 1(a) plots the $G(r)$ of experimental and VASP cal-

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FIG. 1. (Color online) (a) Pair correlation functions $G(r)$ obtained by VASP-MD using $\text{Cu}_{82}\text{Zr}_{46}$ and $\text{Cu}_{79}\text{Zr}_{49}$ clusters with 128 atoms, compared with experimental results respectively. (b) Three typical icosahedronlike clusters, Cu_8Zr_5 , Cu_7Zr_6 , and Cu_9Zr_4 , randomly extracted from $\text{Cu}_{82}\text{Zr}_{46}$ final atomic configuration.

culated results for $\text{Cu}_{64.5}\text{Zr}_{35.5}$ and $\text{Cu}_{61.8}\text{Zr}_{38.2}$ MGs, showing agreement with each other. Using Voronoi tessellation method with a cutoff distance of 3.4 Å,²⁰ it is found that icosahedronlike clusters, e.g., Cu_8Zr_5 , Cu_7Zr_6 , and Cu_9Zr_4 centered by Cu atoms, as shown in Fig. 1(b), are the major polyhedra in both MGs of about 29.7% in $\text{Cu}_{82}\text{Zr}_{46}$ and 28.9% in $\text{Cu}_{79}\text{Zr}_{49}$. Figure 2(a) demonstrates the pair distribution functions $G(r)$ of two MGs together with the difference in $G(r)$, i.e., $\Delta G(r) = G(r)$ (for $\text{Cu}_{64.5}\text{Zr}_{35.5}$) - $G(r)$ (for $\text{Cu}_{61.8}\text{Zr}_{38.2}$). It is clear that the shell numbers of these two MGs are almost the same. However, coordination numbers (CN) in each shell are slightly different. On the first nearest-neighbor shell, from the curve of difference, the intensity increases at the distance of about 2.7 Å and decreases at the distance of about 3.3 Å, corresponding to the increase of Cu-Cu pairs (rather than Cu-Zr pairs, which was confirmed by the EXAFS data analysis) and decrease of Zr-Zr pairs in $\text{Cu}_{64.5}\text{Zr}_{35.5}$ as compared with $\text{Cu}_{61.8}\text{Zr}_{38.2}$, respectively. The peak positions in $\Delta G(r)$ are located at the left side of maxima in $G(r)$, implying a denser atomic arrangement in $\text{Cu}_{64.5}\text{Zr}_{35.5}$ MG than in $\text{Cu}_{61.8}\text{Zr}_{38.2}$ MG. In order to get more reliable atomic structural configuration, we performed RMC simulation *simultaneously* by using three experimental data [one $S(q)$ and two EXAFS spectra]. The simulation box contains 10 000 atoms, which is much larger than 128 atoms for the *ab initio* molecular dynamics simulation. The length of box was used to be 53.218 Å for $\text{Cu}_{64.5}\text{Zr}_{35.5}$ and 53.552 Å for $\text{Cu}_{61.8}\text{Zr}_{38.2}$ MG. The cutoff distances of Cu-Cu 2.3 Å, Cu-Zr 2.45 Å, and Zr-Zr 2.8 Å were adopted throughout the simulation runs. Figures 2(b) and 2(c) display the comparison in $S(q)$ and EXAFS spectra (Cu and Zr K edge) of experimental data (solid line) with simulated ones (dotted line) for $\text{Cu}_{64.5}\text{Zr}_{35.5}$ MG, respectively, showing good agreements between them. Similar fitting results were also obtained for $\text{Cu}_{61.8}\text{Zr}_{38.2}$ MG (not shown here). The agreement of results obtained from RMC and VASP simulations with experimental ones makes it possible to reveal 3D atomic structures for both MGs in Fig. 2(d).

FIG. 2. (Color online) (a) Pair distribution functions $G(r)$ for $\text{Cu}_{64.5}\text{Zr}_{35.5}$ and $\text{Cu}_{61.8}\text{Zr}_{38.2}$ MGs, and the difference between them. (b) Comparison in $S(q)$ and (c) in EXAFS spectra of experimental data (solid line) with RMC simulated data (dotted line) for $\text{Cu}_{64.5}\text{Zr}_{35.5}$ BMG, respectively. (d) 3D atomic configurations for both MGs.

To further deduce local structure of clusters, Voronoi method by setting a cutoff distance of 3.4 Å was also employed. Total fractions of various clusters centered by Cu and Zr atoms with different coordination numbers in these two MGs are shown in Fig. 3 while clusters with their fractions less than 1% are not considered. It is clear that icosahedronlike clusters with CN=12 are dominant in both MGs, in good agreement with the results obtained by *ab initio* molecular dynamics simulation. Most of them with CN=12 are icosahedronlike or distorted icosahedra with index of $\langle 0, 2, 8, 2 \rangle$ and $\langle 0, 3, 6, 3 \rangle$. The amount of the ideal icosahedron of $\langle 0, 0, 12, 0 \rangle$ is rather low. In addition, $\text{Cu}_{61.8}\text{Zr}_{38.2}$ contains slightly more polyhedra with CN=10 and 11 but less in CN=13 and 14 than $\text{Cu}_{64.5}\text{Zr}_{35.5}$ MG. From atomic configurations obtained from RMC, the “quasiequivalent” clusters are deduced and packed to fill the 3D space in these two MGs by face, edge, and vertex sharing. It is found that the medium-range order changes from atom to atom. However, the medium-range atomic packing, i.e., icosahedra companying with polyhedra in relative high coordinates, such as Cu_9Zr_5 , etc., is often found in $\text{Cu}_{64.5}\text{Zr}_{35.5}$ BMG while in $\text{Cu}_{61.8}\text{Zr}_{38.2}$ MG the atomic packing, icosahedra companying with rela-