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EXAFS and molecular dynamics simulation studies of Cu-Zr metallic glass: Short-to-medium range order and glass forming ability

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ABSTRACT

Atomic structures of $Cu_{100-x}Zr_x$ (x = 41.18–66.67) metallic glasses were investigated by extended X-ray absorption fine structure (EXAFS) spectroscopy and molecular dynamics (MD) simulations. It is demonstrated that both the fraction and average volume of the typical atomic clusters, characterized by Voronoi cells, are of compositional dependence. With the increasing of Zr content, the fraction of Cu and Zr centered Voronoi clusters with coordination number lower than 11 and 14 respectively increases, while that of clusters with larger coordination numbers reduces. Among the major Voronoi clusters, the Cu-centered icosahedra are distinctive. Their average volume is far smaller than that of the other Cu-centered Voronoi cells with the same coordination number. More importantly, they prefer to interlink into pentagon-rich icosahedral super-clusters. However, compared with their neighbors, the glasses with x = 44 and x = 50 exhibit no other particularity in Cu-centered icosahedra than a slightly enhanced interlink at x = 50 although glass forming ability (GFA) reaches a local maximum at these two compositions, indicating that there are other factors dominating the GFA change with composition. A significant reduction in free volume for the loosely packed regions takes place at x = 44 and x = 50, due to which the corresponding Cu-Zr metallic glasses have the maximum microhardness.

1. Introduction

Metallic glasses (MGs) lack long-range structural periodicity but inherently possess pronounced short-range order (SRO) and medium-range order (MRO) [1–6], which endow these materials with exceptional functional and mechanical properties [7–12]. Consequently, their atomic-level structures have attracted extensive attention during the past decades, and many structural models such as hard-sphere dense-random packing model [13], stereochemical mode [14], efficient cluster packing model [1], quasi-equivalent clusters model [2] and predictive structural model [15] have been proposed. Meanwhile, numerous efforts were made to experimentally detect or theoretically simulate the microstructure of metallic glasses [16–27].

The Cu-Zr alloy system, as one of the few binary systems that can be solidified into bulk metallic glasses, is an ideal object in this regard. Its best glass forming ability (GFA) locates at several separate narrow compositional ranges. A deviation of no > 1 at.% from the optimal glass-forming composition may significantly change the GFA [28–31], as found in some other alloy systems [32,33]. Conventional criteria on GFA have been attempted to explain the variation in the GFA of Cu-Zr alloys, yet none of them turned out to be a universal indicator [30]. Attentions were then returned to identify the GFA origin from the atomic-scale structure of metallic glasses. In this regard, Sha et al. [34] simulated the $Cu_{100-x}Zr_x$ (x = 35.5–50.0) metallic glasses, and found that the alloy corresponding to local maximum GFA shows a weak yet distinct peak in the fraction of Cu-centered full icosahedra (f_{ico}). They thus concluded that the GFA correlates with the existence of icosahedra, it is however noticed that similar peaks of f_{ico} also appear at some other compositions (x = 36.6, 34.7) where GFA do not exhibit any abnormity [34]. Yang et al. [35] examined the atomic-scale structure of Cu-rich $Cu_{100-x}Zr_x$ (x = 38.2–34.5) metallic glasses, confirming that $Cu_{64}Zr_{36}$ metallic glass which has a local maximum in GFA has similar f_{ico} as its

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adjacent compositions. They therefore proposed that the relatively high atomic packing efficiency of clusters and regularity of the Voronoi cells, rather than f_{ico}, should be responsible for the high GFA in $Cu_{64}Zr_{36}$ metallic glass. Li et al. [36] analyzed the MROs in $Cu_{100-x}Zr_x$ (x = 35, 50) metallic glasses using a cluster correlation method. A strong spatial correlation of Cu-centered icosahedral clusters was detected in these two metallic glasses, and such MRO was believed to be responsible for the glass formation. However, it is known that $Cu_{65}Zr_{35}$ is not a good glass former. In short, despite the intensive investigations, the intrinsic origin pertinent to the high GFA for some Cu-Zr alloys is not well understood yet. The purpose of this paper is to unveil whether the microstructure can serve as a universal indicator for the high sensitive compositional dependence of GFA in Cu-Zr binary metallic glasses by systematically investigating the short- and medium-range orders in a wide range of composition.

Among the various experimental techniques to acquire structural information of materials [18,37–39], extended X-ray absorption fine structure (EXAFS) is a powerful tool that enables the analysis of local structure around selected species [37]. Alternatively, molecular dynamics (MD) simulations based on empirical potentials provides another indispensable approach to examine the atomic structure of metallic glasses. It enables one to construct the three-dimensional structure and make detailed statistical analysis of the structural information. A combination of EXAFS and MD simulation techniques is an effective way to resolve the atomic-scale structure of metallic glasses. In this work, the atomic structures of $Cu_{100-x}Zr_x$ (x = 41.18, 44, 50, 66.67) metallic glasses were firstly investigated by both EXAFS experiments and MD simulations. Based on the good agreements between the MD simulation and experimental data, MD simulations were extended to other $Cu_{100-x}Zr_x$ alloys (x = 41.18–66.67), within which a metastable intermetallic compound CuZr, two stable intermetallic compounds $Cu_{10}Zr_7$ and $CuZr_2$, and two eutectic points can be found on an equilibrium phase diagram [40]. The composition range investigated is much wider than previous investigations, and the simulated atomic configurations are analyzed statistically by employing a weighted Voronoi tessellation method [41,42]. From the composition dependent population of various Voronoi cells (VCs), Voronoi volume, chemical short range order, and partial pair distribution functions, there does not exist any evidence to support the theory that the change of GFA with composition in Cu-Zr alloys is dominated by the short and medium range orders. Interestingly, we found an apparent reduction of “soft region” at local high-GFA compositions, in consistence with their relatively high microhardness.

2. Experimental and Computational Methods

The $Cu_{100-x}Zr_x$ (x = 41.18, 44, 50, 66.67) alloy ingots were prepared by arc melting mixtures of pure Zr (99.9%) and Cu (99.99%) in a Ti-gettered high-purity argon atmosphere. The alloy ingots were remelted five times to ensure chemical homogeneity. Amorphous ribbons of ~40 μm thickness were produced from the alloy ingots using a single-roller spinning apparatus in a high-purity argon atmosphere. The amorphous nature of the as-quenched ribbons was confirmed by X-ray diffraction (XRD) and differential scanning calorimetry (DSC), as described in our previous work [31].

The extended X-ray absorption fine structure (EXAFS) measurements were performed at the beamline BL-14W1 of the Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China), with an electron beam energy of 3.5 GeV and a beam current of 140–210 mA. The incident X-rays were monochromatized by a Si (111) double-crystal monochromator. Zr K-edge and Cu K-edge EXAFS spectra for all samples were collected in transmission mode under ambient temperature. The energy calibration was performed using standard Zr and Cu foils. The thicknesses of the samples were optimized to obtain suitable absorption jumps at each K-absorption edge. All EXAFS spectra were recorded at least twice and averaged subsequently. EXAFS data analyses were performed using the IFEFFIT version 1.2.9 [43]. The EXAFS spectra were extracted using Athena, which were weighted by a weighting factor k^n (n = 3). Then, they were Fourier transformed (FT) into real space through a Hanning window (3.1–11.1 $Å^{-1}$ for Cu K-edge and 3.1–11.0 $Å^{-1}$ for Zr K-edge). EXAFS fits were performed in k-space after filtering out the selected region of coordination shells through a Hanning window (1.6–2.8 Å for Cu K-edge and 1.75–3.25 Å for Zr K-edge) and back Fourier transforming (BFT) into k-space.

MD simulations were carried out for the $Cu_{100-x}Zr_x$ (x = 41.18–66.67) alloys with a composition interval of 1–3 atomic percent by using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [44,45] based on the embedded atom method (EAM) potential developed by Cheng et al. [17]. The simulated box contains 10,976 atoms, with periodic boundary conditions applied in all three directions. During the whole procedure, the pressure was controlled at ~1 bar by employing a Berendsen barostat [46]. The initial configuration of each alloy was heated up to 1500 K and equilibrated for 2 ns with a time step of 1 fs and then quenched down to 300 K at a cooling rate of 10^{11} K/s. The final system was further equilibrated at room temperature for 15 ns. The theoretical EXAFS spectra were evaluated by averaging over the ab initio results from FEFF9 calculations [47] for five hundred clusters centered on Cu or Zr atom picked randomly from the final stage of the equilibrium run.

Based on the atomic trajectories from the MD simulations, partial pair distribution function (PDF) $g_{\alpha\text{-}\beta}(r)$ with α as the central atom and β as the surrounding atom can be calculated according to the following equation [3]:

$$g_{\alpha-\beta}(r) = \frac{V}{4\pi r^2 N_\alpha N_\beta} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \delta(r - |r_{ij}|), \quad (1)$$

where V is the volume of the system, $N_\alpha$and N_β are the number of α and β atoms, respectively. $|r_{ij}|$ is the distance between atom i of type α and atom j of type β. The PDF describes the spatial/radial correlation between a pair of elements α and β. Higher PDF peaks suggest a relatively stronger correlation. When α and β are limited to central atom of specific Voronoi cells, $g_{\alpha\text{-}\beta}(r)$ will reflect the spatial correlation of the Voronoi cells they represent.

The weighted Voronoi tessellation analysis [41,48], which take into account the atomic size difference of constitute elements in a given system, was employed to examine the local environments around each atom in the metallic glasses. The local environment surrounding an atom is well presented by the Voronoi polyhedron enfolding the atom, and is generally labeled by a Voronoi index $\langle n_3, n_4, n_5, n_6\rangle$, where n_i denotes the number of i-edged faces of the Voronoi cell and Σn_i gives the total coordination number (CN). The Voronoi index can be used to designate and differentiate the type of the coordination polyhedron surrounding an atom.

3. Results and Discussion

3.1. Comparison Between Experimental and Theoretical EXAFS Spectra

In EXAFS measurements, the interference of emitted and reflected photoelectron waves can be used to retrieve information about the local environment of the selected atom species, including interatomic distance, coordination number, and structural disorder. Fig. 1 compares the experimentally measured EXAFS to the theoretical ones calculated based on configurations from the MD simulations in typical $Cu_{100-x}Zr_x$ (x = 41.18, 44.00, 50.00, 66.67) metallic glasses. For each composition, the theoretical EXAFS spectrum at Cu/Zr K-edge is obtained by averaging the calculated $\chi(k)$ functions over 500 Cu/Zr-centered clusters picked randomly from the MD trajectories. As seen in Fig. 1(a) and (b), reasonable agreements between the calculated and experimentally measured EXAFS spectra are achieved at both Cu and Zr K-edges in the Cu-Zr metallic glasses, suggesting the reliability of the MD simulations