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Atomic and cluster level dense packing contributes to the high glass-forming ability in metallic glasses

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ABSTRACT

The microstructure features of a representative $Zr_{48}Cu_{45}Al_7$ bulk metallic glass (BMG) were investigated via a series of simulations and calculations coupled with the synchrotron radiation-based experiments. It was revealed that bond shortening occurs in the atomic pairs, due to the strong interaction between the Al dopant atoms and their neighbors. The bond shortening leads to the atomic and cluster level dense packing in the local structures, which should be the structural mechanism of the high glass-forming ability in Al-microalloyed BMGs. This work not only reveals the atomic and cluster level microstructures in this class of glass materials, but also has implications for developing other BMGs with relatively large critical sizes.

1. Introduction

The underlying mechanism of the glass-forming ability (GFA) in alloys is the key for a broad application of these metallic glasses as engineering materials. However, this is a long-standing issue [1–7]. It has been well accepted that the formation and the macroscopic properties of materials are strongly influenced by their microstructures. Thus, great efforts have been devoted to investigating the microstructure in glassy alloys [8–13]. Unlike the crystalline alloys, it is still a challenge to establish the explicit structural pictures in amorphous alloys. So far, it has been realized that clusters (the convex polyhedra made up of one center atom and some shell atoms) should be the building blocks of microstructure in this class of glassy materials, based on which several structural models have been proposed [8–10]. These studies revealed the inherent short-range and medium-range ordering in glassy alloys, by building and stacking clusters topologically and chemically. It also has been suggested in these structural models that the dense packing principle is available for detecting the essential structural nature of glassy alloys, which enhances understanding of the glass-forming mechanism in alloy systems.

Recently, at the macroscopic scale, it has been enunciated that the mass density difference between a glassy alloy to its corresponding crystal alloy reaches the local minimum at a pinpointed composition with the best GFA. This implies that high dense packing efficiency in microstructure may significantly contribute to the relatively high GFA in a composition-pinpointed bulk metallic glass (BMG) [14]. The above-mentioned structural models indicate that dense packing is a universal phenomenon in the glassy alloy, However, in the atomic and cluster level microstructure, it has not been found that how dense the atoms pack in the clusters and how dense the clusters fill in space. Thus, it is difficult to reveal the packing–GFA relationship by using these structural models.

In this work, a series of simulations and calculations coupled with the synchrotron radiation-based experiments were performed to address this issue. A representative $Zr_{48}Cu_{45}Al_7$ BMG and a corresponding $Zr_{50}Cu_{50}$ binary alloy were selected as the research prototypes. $Zr_{48}Cu_{45}Al_7$ has a critical casting size of 8 mm [15], which is higher than that (1.5 mm) of $Zr_{50}Cu_{50}$ composition [16]. It was found that bond shortening caused by strong atomic interactions occurs in the Al-containing atomic pairs, which leads to a relatively high dense packing the atoms in clusters and a high space-filling efficiency of the clusters themselves. The atomic and cluster dense packing is the structural origin of the high GFA in the

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Al-microalloyed glassy alloys. This work may extend to other multicomponent BMGs, and has implications for searching more BMGs with relatively large critical sizes.

2. Experimental and simulation methods

2.1. Synchrotron radiation-based experiments

The selected $Zr_{48}Cu_{45}Al_7$ ternary and $Zr_{50}Cu_{50}$ binary alloy ingots were prepared by arc melting the mixture of Zr (99.9 wt.%), Cu (99.9 wt.%), and Al (99.9 wt.%) elements in Ti-gettered high purity argon atmosphere. The amorphous ribbons having a cross section of 0.04×2 mm^2 were prepared by Melt-spinning on these ingots. The synchrotron radiation-based X-ray diffraction measurements were performed for all samples at the beam line, BW5, of Hasylab in Germany. A high-energy X-ray (about 100 keV) was used in this measurement, ensuring that the diffraction signals have a wide range of values in Q (the wave vector transfer) space. The two-dimensional diffraction raw data were recorded using a Mar345 image plate, and integrated to Q-space data after subtracting its background by program Fit2D [17]. The diffraction data were normalized via software PDFgetX to obtain the structure factor $S(Q)$. Subsequently, after calculating the proper thickness for each measurement, their Zr and Cu K-edge extended X-ray absorption fine structure (EXAFS) spectra were measured at the beam lines BL14W1, in Shanghai Synchrotron Radiation Facility (SSRF) of China, and U7C, in National Synchrotron Radiation Laboratory (NSRL) of China. The measured data were further normalized via a standard procedure, using software Viper [18].

2.2. Reverse Monte-Carlo (RMC) simulation

The RMC simulation technique is an iterative method extensively used for building structural models in disordered systems that agree quantitatively with experimental data (such as the synchrotron radiation-based x-ray diffraction, EXAFS, and neutron-diffraction data). In particular, it is available for glassy alloys [19]. In this work, the synchrotron radiation-based diffraction and EXAFS data were simulated simultaneously, using software RMCA [20]. The initial cubic boxes containing 40,000 random-distributed Cu, Zr, and Al atoms were built, matching the $Zr_{50}Cu_{50}$ binary and the $Zr_{48}Cu_{45}Al_7$ ternary compositions. During the RMC simulation, the experimental diffraction and EXAFS data were compared with the simulation spectra using the iterative calculation expression [21]:

$$\delta^2 = \frac{1}{\varepsilon^2}\sum_n \left(S_m(Q_n) - S_{exp}(Q_n)\right)^2 + \frac{1}{\varepsilon_{Cu}^2}\sum_n \left(\chi_{m,Cu}(k_n) - \chi_{exp,Cu}(k_n)\right)^2 + \frac{1}{\varepsilon_{Zr}^2}\sum_n \left(\chi_{m,Zr}(k_n) - \chi_{exp,Zr}(k_n)\right)^2 \quad (1)$$

where δ^2 denotes the deviation between the experimental and simulation data, the ε parameters can regulate the weight of the data set given in the fitting procedure, the $S(Q)$ and $\chi(k)$ parameters are the XRD structural factor and the EXAFS signal, respectively. Once an experiment-simulation convergence is obtained, the simulation is stopped, and all the atoms are "frozen" with determined three-dimensional positions in the cubic box. As a result, an atomic-structural model is obtained, which is available for further analyses.

2.3. Voronoi tessellation

According to the Voronoi original algorithm [22], each convex Voronoi polyhedron (VP) is formed by connecting the perpendicular bisectors between a center atom and all of its neighboring atoms. A VP is usually indexed as <n3,n4,n5,n6,…>, where *ni* denotes the number of i-edged faces on its surface. Each VP is

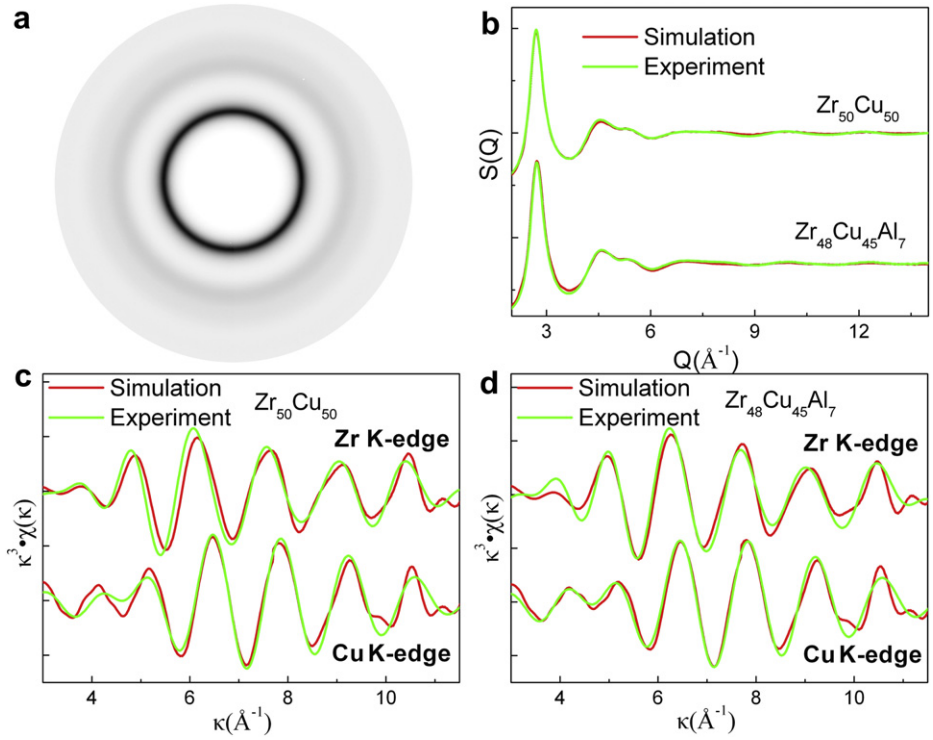

Fig. 1. (a) The two-dimensional diffraction pattern of $Zr_{48}Cu_{45}Al_7$, (b) the structure factor $S(Q)$ of $Zr_{48}Cu_{45}Al_7$ and $Cu_{50}Zr_{50}$, (c) the Zr and Cu K-edge EXAFS spectra of $Zr_{50}Cu_{50}$, and (d) the corresponding EXAFS data in $Zr_{48}Cu_{45}Al_7$. The red and green solid lines denote the simulation and experimental data, respectively. (For interpretation of colour in this figure legend, the reader is referred to the web version of this article.)