Investigation on the atomic structural evolution of as-prepared and annealed ZrCuAl metallic glasses

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Atomic structures of the $\text{Zr}_{48}\text{Cu}_{45}\text{Al}_7$ as-prepared and annealed metallic glasses (MGs) were investigated by performing the reverse Monte Carlo simulation on the synchrotron radiation-based experiments. It was found that although the annealed sample remains completely amorphous, the volumes of the Al-centered clusters evidently expand, which is attributed to the relatively longer Al–Zr bonds. As a result, the role of Al atoms as the glue atoms to connect and fix the Zr- and Cu-centered large clusters is accordingly weakened, which leads to the ease of the rearrangement of atoms and clusters in the glass state. This study provides an insight into the microstructures of MGs, which extends understanding of the structural evolution in the glass alloys during annealing prior to the precipitation of nanocrystals.

I. INTRODUCTION

As a class of amorphous materials, the metallic glasses (MGs) have been attracting increasing interest in recent years because they possess scientific and engineering significance due to their unique properties.^{1,2} Unfortunately, these MGs have encountered a challenge to be widely used in engineering because of their limited casting size, unsolved problem about the glass-forming mechanism, expensive cost, and so on.¹ However, it is found that the precipitation of nanocrystals in the amorphous alloys can improve their properties,³ such as the good soft magnetic property⁴ and high strength,⁵ which may extend their application as engineering materials. Therefore, vast efforts have been devoted to searching for the relationship between the amorphous/nanocrystal structure and their unique properties.^{6–10} So far, amorphous/nanocrystal composite materials can be prepared via the thermal synthesis,¹¹ the mechanical processing,¹² and the electron irradiation¹³ upon MGs. In particular, as a thermal synthesis method, annealing treatment was largely used to prepare these materials, which also is available for probing the phase transformation kinetics and mechanism of the nanocrystallization in amorphous alloys.^{14–16} Whereas, the structural evolution of amorphous-to-nanocrystallization change is far from being clarified, especially whether and how structural evolution occurs in the glasses during annealing prior to the precipitation of nanocrystals is a long-standing issue.¹⁷ In this work, a series of state-of-the-art synchrotron radiation-based experiments coupled with simulations were performed to address this issue, by investigating the structural

evolution of the $\text{Zr}_{48}\text{Cu}_{45}\text{Al}_7$ amorphous alloy,¹⁸ which is a representative bulk MG with unique engineering and structural significance.

II. EXPERIMENTS AND SIMULATIONS

The $\text{Zr}_{48}\text{Cu}_{45}\text{Al}_7$ alloy ingot was prepared by arc-melting the mixtures of Cu (99.9 wt%), Zr (99.9 wt%), and Al (99.9 wt%) elements in Ti-gettered high-purity argon atmosphere, which was melted at least five times to ensure its compositional homogeneity. The corresponding amorphous ribbons with a cross section of $0.04 \times 2 \text{ mm}^2$ were obtained from the master alloys by single-roller melt spinning at a wheel surface velocity of 40 m/s in purified Ar atmosphere. Then, the annealing treatment was carried out in an oven with a vacuum of 10^{-4} Pa at 598 K for 3 min. This temperature is much lower than its glass transition temperature (708 K).¹⁸ Subsequently, the synchrotron radiation-based high-energy (about 100 keV) x-ray diffraction measurements were performed upon the as-prepared and annealed ZrCuAl samples at the beam line, BW5, at HASYLAB (Hamburg, Germany). The two-dimensional diffraction data were recorded using a Mar345 image plate. In addition, using the transmission mode, their Zr and Cu K-edge extended x-ray absorption fine structure (EXAFS) spectra also were measured at the beam line, BL14W1, in the Shanghai Synchrotron Radiation Facility of China. EXAFS did not allow to measure the Al-centered local structure because of the rather low and experimentally inaccessible energy value of the Al K-edge (1.560 keV). Both of the diffraction patterns and EXAFS spectra were normalized via a standard data reduced procedure,¹⁹ employing the softwares PDFgetX and VIPER, respectively. To ensure the reliability of the deduced atomic structural information, both of the normalized diffraction and EXAFS

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data were simulated simultaneously under the framework of reverse Monte Carlo (RMC).^{20,21} Two cubic boxes containing 40,000 atoms were built to simulate these two sample sets, matching the selected $\text{Zr}_{48}\text{Cu}_{45}\text{Al}_7$ composition. Finally, both of the simulated atomic structural models were further analyzed by the Voronoi tessellation method.^{22,23}

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the experimental structural factor $S(Q)$ obtained from the diffraction measurement, Zr and Cu K-edge EXAFS data of the as-prepared and annealed $\text{Zr}_{48}\text{Cu}_{45}\text{Al}_7$, along with their corresponding simulated curves. Except for the first strong peak, the smooth experimental $S(Q)$ curves exhibit the gentle oscillations, and with no sharp peaks, which indicate the full amorphous nature in both samples. The plots of their experimental $S(Q)$ and Cu EXAFS curves are almost the same. However, a slight k-shift and intensity difference of the oscillations between the experimental Zr EXAFS data of both samples are observed, which suggest that the local structure around the Zr atoms changes when the annealing treatment is performed on the ZrCuAl MG. To get more direct structural information, the partial pair distribution function $G(r)$ s are deduced and plotted in Fig. 2 (Cu–Cu, Cu–Al, and Al–Al $G(r)$ s are not shown here). It is found that there is no obvious difference in the Zr–Zr, Zr–Cu, Cu–Cu, Cu–Al, and Al–Al $G(r)$ s for both samples. However, an evident discrepancy ranged from 2.2 to 3.5 Å is observed in the first-shell distribution (FSD) of the Zr–Al pair, which is highlighted in the inset. The FSD is split into two subpeaks (S1 and S2) in the as-prepared ZrCuAl, which possess the peak values at 2.55 and 3.00 Å, respectively. However, in the annealed sample, the FSD is mainly attributed to the relatively strong S1 peak, whose peak value shifts to a higher value (2.70 Å), and the intensity of the S2 subpeak is much lower. It indicates that compared with those of the as-prepared ZrCuAl, most of the Zr–Al pairs possess the similar and longer bond length (2.70 Å) in the annealed sample, leading to the change of the short-range ordering. In addition, because the concentration of Zr around Al is much higher than that of Al around Zr, it is suggested that the change of the Al-centered local ordering is more obvious than that of the Zr-centered counterpart.

To further address this issue, the RMC-simulated atomic structural model is further analyzed at the cluster scale. Figures 3(a)–3(c) show the Zr-, Cu-, and Al-centered major Voronoi tessellation clusters, which have the broad distributions with the coordination numbers ranged from 8 to 14. A slight tendency is observed compared with those in the as-prepared ZrCuAl, the large Al-centered clusters (such as $\langle 0,2,8,2 \rangle$, $\langle 0,2,8,1 \rangle$) possess the relatively high weights in the annealed sample, and the small Al-centered ones (such as $\langle 0,3,6,0 \rangle$ and $\langle 0,4,4,1 \rangle$) have the lower

FIG. 1. (a) Structure factor $S(Q)$ and (b) Zr and Cu K-edge extended x-ray absorption fine structure spectra in the as-prepared and annealed $\text{Zr}_{48}\text{Cu}_{45}\text{Al}_7$ metallic glasses. The solid and dotted lines denote the experimental and simulation data, respectively.

FIG. 2. Partial pair distribution function $G(r)$ s. Zr–Al, Zr–Zr, and Zr–Cu pairs are plotted here. The dotted and solid lines stand for the as-prepared and annealed samples, respectively.

fractions. Such a tendency is not obvious in the distributions of Zr- or Cu-centered clusters. It also indicates that the structural evolution mainly starts around the Al atoms when

FIG. 3. Distribution of the major Voronoi clusters centered with (a) Zr, (b) Cu, and (c) Al atoms.

the glassy alloy is under annealing. Moreover, the volumes of the random atom-centered clusters are calculated for both samples, whose distributions are plotted in Fig. 4(a). It is

FIG. 4. Distribution of the volumes of the Voronoi clusters centered with (a) a random atom and (b) an Al atom.

shown that there is no statistical change in the volume distributions, which means that on average, the present annealing leads no obvious change in the local structural ordering. Nevertheless, the random atom-centered clusters cannot be regarded as the backbones of glassy structure, while the solute-centered clusters are recognized as the basic building blocks to enable the formation of the short-to-medium range ordering.^{24,25} The Al atoms should be the solutes considering its relatively low concentration in both samples, thus, the volumes of the Al-centered clusters also are calculated and plotted in Fig. 4(b). It is worth noting that the large clusters (with a volume larger than 50 Å³) have the relatively high weights in the annealed sample, which indicates that the annealing treatment leads to the expansion of the Al-centered clusters. We have revealed that the average Zr–Al bond length is longer in the annealed ZrCuAl MG than that of the as-prepared sample, which should be the origin of the volume expansion in the Al-centered clusters.

In addition, we compared the representative clusters in the annealed sample with those deduced from the possible precipitated nanocrystalline phases after annealing,^{26,27} as plotted in Figs. 5(a) and 5(b). The method to extract clusters in crystal phases refers to our previous work.²⁸ It is shown that the Voronoi tessellation clusters in Fig. 5(a) are closed convex polyhedra formed by a set of Delaunay tetrahedra with the common vertex at their center atoms, and their surfaces should be only made up of triangle faces.²⁹ These

FIG. 5. Configurations of some representative clusters from (a) the annealed sample and (b) the possible precipitated nanocrystalline phases after annealing. The blue, red, and purple spheres represent the Zr, Cu, and Al atoms, respectively. In particular, in (b), the left, the center, and the right are the clusters extracted from the AlCu_2Zr , the CuZr_2 , and the Al_3Zr crystal phases, respectively. Not all the clusters extracted from the glass alloy and the crystal phases are shown here.

clusters have abundant 5-fold-rotation symmetry features, which are favored in the glass state.³⁰ However, most of the clusters extracted from the crystals cannot be indexed using the Voronoi tessellation method because their surfaces are made up of the quadrangles beside the triangles. Although the others have the Voronoi tessellation indexes, they are rarely found in the glasses, such as the $\langle 0,6,8,0 \rangle$ cluster illustrated in Fig. 5(b). It indicates that the clusters in the annealed glass are different with those in the crystal alloys, i.e., the transition of the glass-favored clusters to those favored in corresponding crystals is absent.

In our previous work,³¹ it has been suggested that in the as-prepared ZrCuAl MG, the relatively short Zr–Al bond attributing from their strong atomic interaction leads to formation of the relatively small and compact Al-centered clusters in the as-prepared ZrCuAl MG. These Al atoms can be regarded as the glue atoms, which occupy the interstices around the Zr- and Cu-centered large clusters to connect and fix them. Accordingly, it strengthens the glassy structure to bypass the crystallization during quenching. It is the structural origin of the enhanced glass-forming ability in the ZrCu alloys with the Al microalloying element. In the present work, it is revealed that compared with that of the as-prepared sample, the Zr–Al pair of the annealed ZrCuAl has a longer bond length, which indicates that the Al–Zr atomic interaction is relatively weakened, and, accordingly, the neighbor atoms are relatively loosely packed around the Al centers to form clusters with the larger volumes. Although in the present annealed sample, the direct transition of the glass-favored clusters to those favored in

corresponding crystals is absent, the expansion of the Al-centered clusters leads to the enhanced motility of Al atoms and their neighbor atoms. The role of Al atoms as the glue atoms to connect and fix the Zr- and Cu-centered large clusters is accordingly weakened, i.e., it decreases the stability of the cluster favored in the glass state. We suppose that once more energy is provided during annealing, the clusters are more unstable and prone to collapse or transform into the crystal-favored clusters, leading to the precipitation of nanocrystal in the amorphous alloys.

IV. CONCLUSIONS

In summary, the atomic structural evolution of the as-prepared and annealed ZrCuAl MGs is investigated. It is revealed that the Zr–Al pair has a longer bond length in the annealed ZrCuAl sample, which is attributed from their relatively weakened atomic interaction. It leads to expansion of the Al-centered clusters. Thus, the motility of the Al atoms and their neighbor atoms are increased, which decreases the connection and stability of their neighbor Zr- and Cu-centered clusters. Thus, it may ease the rearrangement of clusters and atoms in the glass state. The present work not only addresses the issue that how the microstructure changes in MGs during annealing but also has implication for understanding on the mechanism of the precipitation of nanocrystals in glassy alloys.

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