Article

Ab Initio Molecular Dynamics Study of the Structure and Properties of Nb-Doped Zr-Cu-Al Amorphous Alloys

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Abstract: In this paper, experiments were carried out on (Zr0.5Cu0.4Al0.1)100−xNb x (x = 0, 3, 6 at.%) amorphous alloys, and the corresponding ab initio molecular dynamics simulation was performed. The results showed that stable structures of Nb-centered and Al-centered icosahedral (like) atomic clusters were formed after a small amount of (3 at.%) Nb was added. Stable and close-packed backbone structures were formed by the means of interconnection and matching of the two kinds of stable clusters in the alloys, which also enhanced the overall heterogeneity of the structures, thereby improving the strength and macroscopic plasticity. In addition, when more (6 at.%) Nb was added, the stable Al-centered clusters were replaced by some stable Nb-centered clusters in the alloys, and the stability and heterogeneity of the structures were partly reduced, which reduced the strength and macroscopic plasticity.

Keywords: metallic glass; atomic structure; mechanical property; molecular dynamics

1. Introduction

Bulk amorphous alloy also known as bulk metallic glass (BMG) exhibit ultrahigh strength, high hardness, high elasticity, and excellent corrosion resistance [1]. However, the applications of many BMG systems are still limited owing to their room-temperature brittleness and low glass-forming ability (GFA) [2]. ZrCu-based BMGs with high GFA, relatively high room-temperature compression plasticity [3], low cost (no precious metals) and low toxicity have promoted the application of BMGs in a wide range of areas, such as consumer electronics, sports equipment, and biomedical instruments [4–7].

Due to their formation and properties being very sensitive to the types and contents of constituent elements, some properties of ZrCu-based BMGs can be dramatically changed by doping Nb elements [8–19]. In the (Cu46Zr43Al7)100−xNb x (x = 0, 1, 3, 6, 9 at.%) BMGs, the best room-temperature plasticity, and the highest fracture strength and glass transition temperature (T g) are presented when x = 3 [1]. Similar conditions were also observed in the experiments of the Zr-Cu-Al(Nb) BMGs in this paper, as shown in Figures 1 and 2. In addition, Chen et al. [12] found that the plastic strain of the Zr60.5Cu17.5Ni13.5Al8.5 BMG at room temperature is improved from 2% to 20% when only 0.5 at.% Nb is added, and it was observed under a scanning electron microscope (SEM) that multiple shear bands are formed on the fracture surface of the alloy. Cao et al. [13] discovered by experiments that after 2 at.% Nb is added, the critical diameter of the Zr47Cu44Al9 BMG is increased from 4 mm to 10 mm, and the plastic strain is greatly increased to 13.2%. The macroscopic plasticity of the alloy will be reduced if the content of Nb is increased continuously. Jiang et al. [18] studied Cu46Zr48−xAl x Nb x (x = 0, 0.3, 0.8, 1.2, 1.5, 2.0 at.%) bulk metallic glass composites (BMGC) and found a BMGC possessing an excellent combination of high strength (~1.3 GPa), and
significant tensile plasticity (~8%) was obtained by adjusting Nb content (0.3–0.8 at.%). Wu et al. [19] explored Cu_{50.2}Zr_{40.8}Ti_{9−x}Nb_{x} (x = 0.5, 1, 2 at.%) BMGs and composites via experiments, found that as-cast alloys with 1.0 at% of Nb element display the large time window of serrated events, implying that the serrated behavior can dynamically retain in a long-time scale and thus the alloy is endowed the largest compressive plasticity.

These experimental results demonstrate that the internal structure of ZrCu-based BMGs can be changed significantly by adding a little Nb (less than 3%), thus improving the macroscopic plasticity, but too much Nb added will reduce the plasticity and strength of the alloys. Generally, it is difficult to simultaneously guarantee the plasticity and strength of materials in the same alloy system, and the increase in plasticity is usually accompanied by the decrease in strength, and vice versa. However, the strength and plasticity of Zr-Cu-Al BMGs added with a small amount of Nb can be enhanced simultaneously [8,13], showing an unclear micro-mechanism yet. As a result, this problem was studied in this paper in combination with the experimental results and ab initio molecular dynamics (AIMD) simulation and based on the analysis of atomic structures of alloys.

2. Experimental and Simulation Methods

Alloy ingots with nominal composition (Zr_{0.5}Cu_{0.4}Al_{0.1})_{100−x}Nb_{x} (x = 0, 3, 6 at.%) were prepared by arc-melting high-purity elements under an argon atmosphere. For convenience, we labelled them as Nb0, Nb03 and Nb6, respectively. Bulk glassy samples with a diameter of 2 mm were prepared by copper-mold suction casting. The structures of the as-cast specimens were examined by X-ray diffraction (XRD) using Cu-Kα radiation at tube voltage of 40 kV and tube current of 30 mA. Thermal stabilities of the samples were examined by differential scanning calorimetry (DSC) at a heating rate of 40 K/min. The
specimens with a diameter of 2 mm and a height of 4 mm were tested in compression under a strain rate of $5.0 \times 10^{-4}$ s$^{-1}$ at room temperature.

In order to investigate the micro-structure of the $(\text{Zr}_{0.5}\text{Cu}_{0.4}\text{Al}_{0.1})_{100-x}\text{Nb}_x$ (x = 0, 3, 6 at.%) BMGs and the micro-mechanism of its mechanical behavior, AIMD simulation and analysis were carried out on the rapid cooling and glass transition processes from 2000 K to 300 K of the molten alloys using $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ (Nb0), $\text{Zr}_{48}\text{Cu}_{39}\text{Al}_{10}\text{Nb}_3$ (Nb3) and $\text{Zr}_{47}\text{Cu}_{38}\text{Al}_{9}\text{Nb}_6$ (Nb6). Our AIMD simulations of the amorphous structures of the alloys are conducted by using the Vienna ab initio Simulation Package (VASP) (5.2, VASP Software GmbH, Sensengasse 8/12, A-1090, Vienna, Austria) [20,21]. The temperature is controlled using the Nose–Hoover thermostat. The Brillouin zone integrations are carried out using only the $\Gamma$-point. The projector augmented wave (PAW) method and Perdew–Burke–Ernzerhof (PBE) functional are used to describe interacting valence electrons [22,23]. All computations were performed with a cutoff energy of 355 eV. The equation of motion was solved via the velocity Verlet algorithm with a time step of 3 fs. A cubic supercell with 100 atoms with periodic boundary conditions (PBCs) was initially constructed according to the experimental density. First, a well-equilibrated liquid configuration was established after running 9 ps at a temperature as high as 2500 K. Then the ensemble was sequentially equilibrated for 9 ps at each of the temperatures: 2000, 1700, 1500, 1300, 1100, 1000, 900, 800, 700, 600, 500, 400 and 300 K. Three thousand configurations were collected at each temperature and only the last one thousand were adopted for structural analysis.

3. Results and Analysis

Figure 1 shows the DSC curves of the as-cast amorphous specimens, the glass transition temperatures of the Nb0, Nb3 and Nb6 are 703 K, 711 K and 707 K, respectively. The compressive engineering stress-strain curves of 2 mm diameter BMG rods are shown in Figure 2. Nb0, Nb3 and Nb6 specimens show the plastic strain ($\epsilon_p$) of 0.87%, 2.63% and 1.71% and fracture strength ($\sigma_f$) of 1876 MPa, 2001 MPa and 1925 MPa, respectively.

3.1. Analysis of Pair Correlation Functions

The partial pair correlation functions (PPCF) of the alloys Nb0, Nb3 and Nb6 at 300 K were obtained by AIMD simulation and calculation, as shown in Figure 3. The shapes, as well as the size and position of the first peak and the first valley of the PPCF curves were relatively close between the main components (Zr-Zr, Zr-Cu and Cu-Cu) of the three alloys, which indicated that the local structures between the main components differ little. By contrast, there were more obvious differences between local structures centered by Al and Nb atoms.

According to Figure 3, the first peak in the PPCF of Al-Al of Nb0 and Nb3 was stable, while that of Nb6 was affected, suffering bifurcation and being flat, which indicated that the relative positions of Al–Al pairs become unstable and are interfered by Nb when the content of Nb was increased to 6 at.%. There was little change in the Al–Zr and Al–Cu pairs, and the relative positions of Nb–Zr, Nb–Cu and Nb–Al pairs were more concentrated with the addition of Nb. In the Nb3 alloy, the first peak of Nb–Nb was near 5 Å outside the first shell since less Nb contact was available due to the low Nb content. In the Nb6 alloy, the Nb–Nb pairs were stably distributed in the first shell, and the first peak was near 2.861 Å, close to the atomic diameter in Nb crystals, presenting strong interaction and a tendency toward agglomeration, which was different from the tendency toward dispersion of Al–Al pairs.
3.2. The Analysis of Mean Square Displacement

To understand the dynamical and structural properties of atoms of the three molten alloys, the mean square displacement (MSD) of the atoms during the cooling process was analyzed. As shown in Figure 4, the MSD curve almost turned to a horizontal curve from an upward oblique line when the alloy system was cooled to 700 K, manifesting that the alloy was changed from the supercooled liquid structure to a solid glass structure at that time. The MSD curves of Nb3 and Nb0 were very close to each other during the cooling process from 700 K to 300 K, proving that the overall atomic diffusion capacity of the two alloys were similar. The MSD curve of Nb6 was significantly higher than that of both Nb0 and Nb3 in most cases, showing a larger slope, which indicated that Nb6 holds stronger mean atomic diffusion capacity and lower viscosity. For alloys with higher viscosity, the atomic motion is more violently hindered by surrounding atoms, and it is more difficult to perform local rearrangement, nucleation and growth. Hence, according to the analysis of all MSD curves, it could be inferred that the glass-forming ability of the alloy system will decline with the increase in Nb content (after more than 3%).
To further know the dynamics performance of all components of the alloys, the MSD curves of all components at 300 K were analyzed. In the alloy system (Figure 5), Cu presented the strongest mean diffusion capacity, followed by Zr, and the two main components basically determined the overall atomic motion capacity of the alloys. Al in the Nb0 and Nb3 alloys had the weakest mean diffusion capacity, indicating that Al is located in the center of stable clusters. The role of Al as the central atom of clusters in Nb6 was further weakened with the continuous increase in Nb content and partly replaced by Nb, which further heightened the MSD curve of Al atoms in Figure 5c and made the curve close to that of all atoms. In spite of similar overall atomic motion capacity of Nb0 and Nb3, the motion capacity differed among components. There was little difference among the mean diffusion capacities of the 4 components of Nb3, which was distinctly different from the conditions of Nb0 and Nb6, proving that an organic and integrally stable structure is formed by the coordination of the components of Nb3.
Figure 5. MSD curves of various elements of the alloy simulated by AIMD at 300 K: (a) Nb0; (b) Nb3 and (c) Nb6.

3.3. Analysis of Bonding Pairs

Figure 6 illustrates the changes of bonding pairs [24] of the most frequent occurrence during the cooling process from 2000 K to 300 K of the simulated Nb0, Nb3 and Nb6 amorphous alloys, which demonstrates the change trends of bonding pairs of the three alloys in cooling. According to Figure 6, the total content of the 1551 and 1541 bonding pairs representing the five-fold symmetrical structure (icosahedral or icosahedral-like structure) accounted for more than half in most conditions, and 1551 was the primary bonding pair, which indicated that this kind of amorphous alloy is dominated by icosahedral (or icosahedral-like) structures and contains less disordered cluster structures, face-centered cubic (FCC), hexagonal close-packed (HCP) and body-centered cubic (BCC) structures. The content of bonding pairs of the three alloys changed differently with the increase in Nb content. According to the previous analysis, the stable cluster of Nb0 was in an icosahedral (or icosahedral-like) structure with Zr and Cu agglomerated around Al, which was overwhelmingly dominated by the 1551 bonding pair. For Nb3, the content of the 1431 bonding pair was obviously increased compared with Nb0, while the content of the 1551 bonding pair was slightly decreased, which revealed that the stable Al-centered cluster structure of Nb0 was partly destroyed or replaced by Nb clusters due to the small amount of Nb added. With the continuous increase in Nb content, the 1551 bonding pair in Nb6 was replaced by some 1541 bonding pairs, further reducing the content of the 1551 bonding pair. The stability of the 1541 bonding pair was significantly lower than that of 1551, because the five bonds of the 1551 bonding pair were closed to each other, while there was one breakage in the 1541 bonding pair. Consequently, the overall stability of the internal structure of Nb6 was not as good as that of Nb3.
Figure 6. Changes of bond pair content in simulated Nb0, Nb3 and Nb6 during cooling from 2000 K to 300 K: (a) Nb0; (b) Nb3 and (c) Nb6.

3.4. Analysis of Free Electron Density

As shown in Figure 7, the free electron probability density contours of clusters in Nb0, Nb3 and Nb6 at 300 K were obtained by AIMD simulation. Metal atoms form cluster structure by bonding with each other through electrons. The greater the electron (probability) density between atoms, the stronger the interaction and the closer the connection. Figure 7 indicates that Nb has strong interaction with all four components, and Al is easy to lose the outer electron and become Al ion. Stable atomic clusters can be formed with Nb or Al as the center. These stable atomic clusters are similar to “superatoms” and can be regarded as basic structural unit [25,26].

Figure 7. Cont.
3.5. Analysis of Voronoi Polyhedra

The content of five kinds of Voronoi polyhedral [27] with the most frequent occurrence in the cooling process of the three simulated amorphous alloys was subjected to statistical analysis, as shown in Figure 8. In the alloys, the Zr- and Cu-centered Voronoi polyhedra were generally unstable, while the Al-centered icosahedral (-like) appeared more frequently in the alloys. According to Figure 8, the content of icosahedral <0, 0, 12, 0> was successively reduced, while the content of icosahedral-like <0, 2, 8, 2> was increased with the increase in Nb. It was revealed that Al and Nb elements are generally the central atoms of the clusters in the amorphous alloy system, similar to “solute” atoms, while Zr and Cu are similar to “solvent” atoms. High stability was presented in Nb-centered Voronoi polyhedra such as icosahedral <0, 0, 12, 0> and icosahedral-like <0, 2, 8, 2>, which indicated that some stable Al-centered icosahedral clusters in the alloys are gradually replaced by stable Nb-centered clusters, changing the original cluster structure of Nb0 in the alloys to a certain extent. The results are consistent with the conclusion in previous analysis.
Figure 8. Changes of Voronoi polyhedron content in simulated amorphous alloys during cooling from 2000 K to 300K: (a) Al-centered in Nb0; (b) Al-centered in Nb3; (c) Al-centered in Nb6; (d) Nb-centered in Nb6 and (e) Nb-centered in Nb6.

The dynamics performance of every atom in the supercell was analyzed, and the distribution of relatively stable clusters in the alloys was obtained (Figure 9) pursuant to the motion of atoms and the analysis of Voronoi polyhedra. With the increase in Nb content, the number of stable Nb-centered clusters (marked in orange) was gradually increased, while that of stable Al-centered clusters (marked in blue) was gradually reduced. Nb3 had more stable clusters than Nb0 and Nb6, and the two types stable clusters of Al and Nb were interconnected in the cell by sharing solute atoms, lowering the overall motion capacity and improving the viscosity, and then affect GFA of alloy. The stable clusters occupied most spaces of the cell and formed a spatial backbone structure, similar to Miracle’s model of the metallic glass dense random cluster packing structure [28,29], resulting in high strength and glass transition temperature [30] (see Figures 1 and 2). Because some other atoms are not completely bonded to each other, this part cannot form a stable dense stacking...
structure, which is an unstable region. This leads to structural heterogeneity. Additionally, the difference in the stability of the two kinds of clusters also promoted the heterogeneity of the internal structure and caused multiple shear bands occur easily, so the macroscopic plasticity was improved in Nb3, as shown in Figure 2.

Figure 9. Distribution of stable clusters (closed polyhedra) in cells of simulated amorphous alloys at 300 K: (a) Nb0; (b) Nb3 and (c) Nb6.

4. Conclusions

AIMD simulation and experiments were carried out on the (Zr0.5Cu0.4Al0.1)100−xNb(x = 0, 3, 6 at.%) BMGs. The results are as follows:

1. Al-centered icosahedral (and/or icosahedral-like) atomic structure are relatively more stable structure of atomic clusters in Zr50Cu40Al10;
2. The structural forms of atomic clusters of the alloys are changed after adding 3 at.% Nb. Nb-centered icosahedral (-like) structures can form relatively stable clusters and coexist with Al-centered icosahedral (-like) structures, and an integrally more stable and close-packed structure can be formed via interconnection and matching of the two stable polyhedra, thereby enhancing the strength of the alloys. The overall heterogeneity of the structures is enhanced due to the two stable clusters, so the macroscopic plasticity of the alloys is improved;
3. After 6 at.% Nb is added, the Al-centered icosahedral (-like) clusters in the alloys are replaced by more Nb-centered icosahedral (-like) clusters, and the stability and heterogeneity of the structures were partly reduced resulting in declined mechanical properties.
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