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Effect of chemical composition and affinity on the short- and medium-range order structures and mechanical properties of Zr-Ni-Al metallic glass

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ABSTRACT

Previous studies have shown that a small variation in the chemical composition of metallic glasses (MGs) can drastically alter their strength and ductility. However, the underlying structural origin and atomistic mechanisms remain unclear. Using large-scale molecular dynamics simulations, we studied the effect of chemical composition and affinity on the microstructure and deformation behaviour of $Zr_{50}Ni_{50-x}Al_x$ MG by varying the value of x in the range of $5 \le x \le 25$ (at.%). We show that an increase in x is able to strengthen and embrittle the material. In particular, a ductile (homogeneous deformation) to brittle (shear banding) transition occurs at $x \sim 15$. To reveal the structural origin, we performed both short- and medium-range order (SRO/MRO) analyses on the MG. By varying the cooling rate while maintaining a constant composition, our structural analyses identify the Al-centred full-icosahedron (Al-FI) as the key structural motif responsible for the strengthening and embrittlement. Then, our analyses of SRO and MRO reveal an increase in both the fraction and connectivity of Al-FI by increasing x from 5 to 25 at.%. We also show that chemical affinities among different atomic species are strongly correlated with the structural attributes, which in turn strongly affect the mechanical behaviour of the MGs. Our findings highlight the importance of chemical composition and affinity in influencing the microstructural features of MGs at different length scales and their mechanical properties.

1. Introduction

Owing to the combination of metallic bonding and lack of translational symmetry, metallic glasses (MGs) exhibit several remarkable properties, such as high elastic limit and resilience, high yield strength and hardness, and near-net-shape processing [1–4]. However, a notorious vulnerability that prohibits MGs from being widely employed in structural applications is their catastrophic failure *via* localized shear banding at room temperature [4–6]. A greater understanding of the atomic structure and resulting failure mechanisms in MGs is currently at the forefront of materials research [1,2].

Recent studies have shown that the mechanical properties of MGs are strongly dependent on their chemical composition [7–17]. For example, an increase in the atomic percentage (at.%) of Cu in Cu_xZr_{100-x} MG from $x = 45$ at.% to 65 at.% is able to increase the yield strength by 500 MPa and reduce the plastic strain from 6% to almost 0 [11]. Another example is that an addition of only 0.5 at.% Fe (or Co) to Zr-Cu-Al MG (with no plasticity) increases the plastic strain from nearly 0 to about 6%, while decreases the yield stress by 35 MPa [15]. To explain the origin of such dramatic changes in the mechanical properties, several mechanisms and models have been proposed, for example nanoscale crystallization [10], nanoscale structural heterogeneities [8,9], spinodal phase transformation [16], and free volume effects [7,18,19]. Currently, there is no consensus on which mechanism is truly responsible for the drastic changes, and this issue remains controversial [17,20–23].

The plasticity of MGs has been empirically associated with Poisson's ratio, ν (or G/B, where G and B are shear and bulk modulus, respectively) [21]. For example, Zr-, Cu-, Pt-, and Pd-based bulk metallic glasses (BMGs) with ν higher than 0.31–0.32 are relatively ductile, while Fe- and Mg-based BMGs with smaller values of ν are brittle [21,22]. Although these trends remain general, there are some deviations from this empirical rule. For example, Pd- and Au-based BMGs, which have $\nu > 0.39$, are still brittle [23,24]. These deviations can be further intensified through altering the atomic structures by simply changing the fabrication history of the MGs (*e.g.* cooling rate) [12,25,26]. Researchers have recently tried to generalize the relationship between ν and plasticity by including the effects of glass atomic structure [12]. Their analyses have demonstrated that mechanical properties of a variety of MG systems cannot be simply described by the rule of mixtures, and the atomic structure of the MG must be taken into account [12].

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The paradigm of "structure-property correlation", which has been very successful in rationalizing and predicting the mechanical behaviour of crystalline alloys, is not as straightforward in their glassy counterparts. This is due to the fact that the microstructure of crystalline materials readily bifurcates into near perfect lattice sites and discrete defects [27]. In contrast, monolithic MGs consist of a continuous spectrum of local structures with no distinguishable microstructural feature [27,28]. Hence, while a cogent atomic theory of plasticity (such as dislocation theory for crystalline matter) remains elusive for MGs, understanding the effect of chemical composition and affinity on the atomic structure and mechanical behaviour of multicomponent MGs clearly is crucial towards designing new MGs and boosting their potential for structural applications [20].

In the current study, we used molecular dynamics (MD) simulations to investigate the effects of chemical composition and affinity on the mechanical properties and atomistic structure of a prototypical ternary Zr-based MG system, *i.e.* Zr-Ni-Al. It is noted that the Zr-based MG alloys exhibit high glass forming ability (GFA), desirable mechanical properties (*e.g.* compressive ductility for bulk samples and tensile ductility for nanosize samples [29]), and consist of common, inexpensive, non-toxic engineering metals [1], making it an ideal system for commercial applications [30,31]. While previous studies primarily focused on the Zr-Cu based systems [12,13,17,32–35], a detailed understanding of ternary Zr-Ni-Al systems is still lacking, especially in the area of atomistic structure and its correlation with mechanical properties [36,37]. Certainly, studies on ternary MGs would provide valuable insights into higher order quaternary and quinary systems [38].

Previous experimental and computational studies have suggested that in order to obtain Zr-based MGs with greater ductility, the alloy must have a higher concentration of solvent element (Zr) [11–13,17]. However, here we show that in a multi-component Zr-based MG, by keeping the concentration of the solvent (Zr) constant, it is still possible to tune the ductility of the system by properly adjusting its minor alloying elements. In our multi-component MG system, we also investigate the composition dependence of the medium-range order (MRO), *i.e.* the connectivity of short-range order (SRO) motifs [39]. This is important since different arrangements of SRO clusters can lead to different mechanical properties [13]. At the most fundamental level, chemical affinity of different atomic species of the glass is responsible for the chemical make-up of the nearest-neighbour shells, *i.e.* chemical short-range order (CSRO). As a result, CSRO affects the connectivity of local structural motifs to form MRO. We quantitatively analyse the effect of chemical composition on the CSRO and its correlations with MRO and mechanical properties of our MG samples. More specifically, in the current work, we would like to answer the following questions:

1- How can the mechanical properties of a multicomponent MG be tuned by adjusting the concentration of its minor alloying elements?
2- Is it possible to identify a SRO motif as the key structural indicator that is correlated with the mechanical behaviour of a MG system?
3- What are the effects of chemical affinity and composition on the SRO, MRO, and CSRO and consequent mechanical properties of the MG?

2. Methods and model

The MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [40]. The interactions between atoms were modelled by adopting embedded atom method (EAM) potentials parameterized for the Zr-Ni-Al system [41]. Five representative $Zr_{50}Ni_{50-x}Al_x$ MGs were prepared, in which x was chosen to be 5, 10, 15, 20 and 25. Each sample consisted of about 10,000 atoms. Hereafter, the corresponding MGs are referred to as S05, S10, S15, S20 and S25, respectively. Each sample was first melted at 2300 K and the liquid was thermally equilibrated at the same temperature for 10 ns. Subsequently, the liquid was quenched to room temperature (300 K) with a cooling rate of 1×10^{10} K/s, and equilibrated at 300 K for another 5 ns. Periodic Boundary Conditions (PBCs) were applied in all three directions (x, y and z) of the samples. The isothermal–isobaric ensemble (NPT) was applied during the melting/quenching processes at zero pressure, where the temperature and pressure of the systems were controlled using a Nose-Hoover thermostat/barostat [42]. Another independent series of MGs with a composition of $Zr_{50}Ni_{30}Al_{20}$ (similar to S20) were also constructed following the same melt/quench procedure but applying different cooling rates of 10^{10} K/s, 10^{11} K/s, 10^{12} K/s, and 10^{13} K/s, which hereafter, are referred to as C10, C11, C12 and C13 samples.

To construct large-scale MG samples for uniaxial tensile tests, the resulting MGs were replicated individually to obtain a large slab with dimensions of about 300 Å × 60 Å × 900 Å in *x*, *y*, and *z* directions respectively, giving an aspect ratio (width:height) of 1:3. For the tensile tests, a uniaxial strain was applied along the *z* direction with a constant engineering strain rate of 4×10^7/s. Periodic boundary conditions were applied along *y* and *z* directions, while a free surface boundary condition was applied along the x direction. The engineering stress was calculated from the Virial atomic stress tensor to obtain the stress-strain curves as the macroscopic mechanical behaviour of the samples [43]. In our simulations, we used the Verlet algorithm to integrate the equations of motions with a time step of 0.001 ps. As a measure of local deformations, the atomic von Mises strain [44] was adopted and the OVITO software package [45] was employed for visualization.

Following the widely used practice in literature, the atomistic structure of our MG samples is characterized by the Voronoi tessellation technique, hereafter called "Voronoi analysis" [46,47] using our own in-house software based on the Voro++ code package [48]. In the Voronoi analysis, the distances between a given central atom and its nearest neighbours are divided by planes at the distances equal to atomic radii. The intersection of these planes with each other forms a polyhedron surrounding each atom. The common nomenclature to denote these polyhedra is a set of indices in the form of $\langle n_3, n_4, n_5, n_6\rangle$, where n_i represents the number of polygonal faces with i vertices. This set of indices is known as the Voronoi index. In this case, for each atom at the centre of a Voronoi cell, the coordination number is: $CN = \Sigma n_i$. For example, a Voronoi index of ⟨0, 0, 12, 0⟩ represents a special Voronoi cell, *i.e.* a regular dodecahedron whose central atom has five-fold bands with all of its 12 nearest neighbours located at the vertices of a full-icosahedron (FI) cluster. Hence, the Voronoi index of a given atom reflects the topological arrangement of its nearest-neighbour shell, which has been widely adopted for characterizing the short-range order (SRO) in metallic glasses [49–52]. Due to the continuous spectrum of local topology in MGs, their atomic structure should be quantified statistically [27]. Here, we note that in other amorphous systems, such as ionic liquids [53], different techniques might be used to analyse their atomistic structure and reveal the corresponding correlations between the structural information and the dynamic and other properties of the materials. Moreover, since MD simulations can provide a 3D picture of the atomistic configuration of MGs, it is a powerful technique to systematically investigate their structure-property correlation, which is otherwise not readily achievable experimentally.

3. Results and discussion

In general, the mechanical behaviour of metallic glasses is controlled by both their chemical compositions and atomistic structure, *i.e.* how the atoms of different constituent elements are bonded and spatially packed in the glassy state [12]. In principle, it should be possible to identify key structural indicators that are responsible for the mechanical behaviour of a glass [12]. In the following, we attempt to identify the key structural indicators of the Zr-Ni-Al system by systematically analysing its atomic structure *via* changing the cooling rate at a fixed composition.

The effect of cooling rate on the macroscopic mechanical behaviour of our Zr-based MG samples at room temperature (300 K) and a fixed composition ($Zr_{50}Ni_{30}Al_{20}$) is presented in Fig. 1(a). This figure presents

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