Local stress analysis in Cu$_{50\%}$Zr$_{50\%}$ metallic glass under shear strain by means of first principle modeling

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Abstract

Metallic glass is highly ductile material, which is very important for industry. Thorough understanding of its mechanical behavior can be achieved only in studies of atomic-level mechanisms of the deformation. In the current work the attempt was made to explain the shear modulus softening in CuZr glassy alloy by means of first principle modeling of Cu$_{50\%}$Zr$_{50\%}$ metallic glass under shear strain. We used \textit{ab initio} local stress calculation technique in order to get insight into the response of individual atoms to the strain. It was shown that Zr subsystem demonstrates very stiff behavior, while the displacements of Cu atoms from their equilibrium positions, induced by the strain, provide the stress drop to Zr atoms and the whole system.

Keywords: Metallic glass, First principle calculations

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1. Introduction

Amorphous materials formed by metal atoms, usually referred to as metallic glasses (MG) or glassy metals, have gained significant attention after in the 1990s the procedure of mass production of the bulk form of such materials had been developed [1, 2]. Moreover appearance of glass-forming alloys, which require relatively low cooling rates of \( \approx 100 \text{ K} \cdot \text{s}^{-1} \) [3], insures broad applications of MGs for industry (to name nanoimprinted technology, bio-implants and coating as a few examples [2, 4]).

Along with applications metallic glasses have received extensive scientific interest. One of the striking differences of MGs from ordered materials is shear modulus softening, which may be up to 30\% lower than the correspondent shear modulus of the crystal [5]. However, mechanical properties of MGs are not well explained yet [6]. In case of crystalline materials an-elastic behavior is governed by defects of the structure. In contrast to crystals, attempts of defining defects in glasses face a formidable barrier of essential randomness of the structure. Nevertheless, a number of theories of deformation in MG was proposed, among which the most advanced one is formulated in terms of so-called shear transformation zone (STZ) [7, 8, 9]. It connects the deformation in amorphous material with the emergence and development of regions with low local shear modulus. Despite advances of the STZ theory, a number of its key features remain unveiled. As an example, such an important property as shear transformation zone size (number of atoms involved)
In particular experiments is defined to values contradictory to each other [10, 11, 12, 13]. Also, particular mechanism of STZ emergence is yet to be understood. In spite of pure heterogenic structure, there can be shown a clear difference between nearest neighbors and other atoms in amorphous structure [14]. Therefore an average value of the bond length could be defined in the structure by analysing the pair-density correlation function (PDF) [15]. However, more sophisticated many-body correlations should be considered in order to elucidate properties of glasses. Such correlations can be seen in Voronoi polyhedra analysis [16, 15], which is usually used to treat a local atomic structure in amorphous materials. Except that conventional approach, slightly different approach was introduced by T. Egami with coauthors [17, 15, 19]. It is focused on the single events of bond breaking/creation rather then the exact position of atom in the structure [20]. Such approach possesses several advantages and, along with atomic-level stress analysis, can be used to link directly the topology of the structure to the physical properties of the material [21].

It can be concluded that the microscopic theory of deformation in metallic glasses is not complete yet. Because of high difficulty of real experiments at atomic-level, the method of choice on that direction is computer modeling [6]. Advances of modern computational methods allow one to obtain an insight into the deformation behavior of the individual atoms. One of the most accurate atomistic modeling methods is based on density functional theory (DFT), which provides the evaluation of structural parameters with accuracy up to 1% [22]. That approach fits well for the purpose of defining the starting point of shear transformation zone in metallic glass, due to the fact that relatively small structures (order of 100 atoms) are appropriate in this case.

In the current work we study Cu₅₀Zr₅₀ under shear strain. The choice of the system is dictated by the fact that big amount of data is already presented for CuZr alloys in both crystalline and glassy structures [23, 21]. It is known that CuZr glass could be obtained in a wide composition range Therefore the influence of the stoichiometry on conclusions of the current work can be studied in further works with possible real experimental approvement afterwards.

This paper is organized as follows. At first the details on structures under study and first principle calculations settings are given. Next, main results are presented and discussed with emphasizing the key properties of the structure leading to the shear modulus softening. Finally, conclusion is made and further studies are suggested.

2. Simulation details

2.1. Equilibrium structure preparation

Initially random atomic configuration of 96 atoms was prepared at a density of 57.1 nm [23]. The first principle molecular dynamics (FPMD) simulation at 3000 K for 2 ps was performed under nve ensemble with periodic boundary conditions to thermalize the initial structure, thus obtaining equilibrium liquid structure. The time step of simulations is 2 fs. In order to obtain relatively stable glass structure the system was quench to a supercooled state with 1200 K, and then FPMD was performed for 1 ps. Then the system was gradually cooled down to a glass state with 700 K at a cooling rate of 0.5 K/fs, and in addition another thermalization at 300 K was performed for 1 ps to stabilize the glass structure. Finally the glass structure was relaxed to 0 K by applying energy minimization.
using conjugate gradient method under macroscopic stress tensor of 0 GPa, allowing the box size and shape to vary during the iterations.

Described procedure allows to obtain an equilibrium structure of the metallic glass ready for subsequent analysis. One of such structures can be seen on the Fig. 1.

![Cu-Zr structure](image)

**Figure 1**: Cu$_{48}$Zr$_{48}$ structure. Blue (green) circles represent Cu (Zr) atoms.

### 2.2. Basic ab initio setup

In our study the quantum mechanical approach in the framework of density functional theory was used, implemented in the Vienna Ab initio Simulation Package (VASP) [24]. The generalized gradient approximation was used for the exchange-correlation energy, which is essential for achievement of high accuracy. The energy cutoff regulating the number of basis functions was set to 410 eV. Because of relatively big size of the system, only Γ k-point was used in reciprocal space. The efficiency of structural optimization was increased by the Methfessel-Paxton method [25] with smearing of 0.1 eV. In the energy minimization process, structures were optimized until atomic forces become less than 0.01 eV/Å.

### 2.3. Modeling of the response to strain

The athermal quasi-static shear (AQS) simulation, which is usually used in the framework of classical MD was performed at the quantum mechanics level using first principle MD. Firstly the glass structure at 0 K obtained by cooling is uniformly deformed with a simple shear strain $\varepsilon_{xy}$ (affine deformation). Next energy minimization allows the positions of atoms to relax with keeping box size fixed, resulting in stress relaxation from affine state during the energy minimization. To improve statistics, four different initial structures, each of which is deformed independently at equal strain but in six different directions, were prepared and the results were totally averaged over 24 samples ($= 4 \times 6$).

In the process of analyzing the mechanical properties of materials under strain, local stress calculations is a common tool to unveil atomic-level correlations. Nevertheless, until recent studies that tool was only available in the classical approximation. Recently
several approaches were proposed allowing calculation of an atomic stress in quantum-mechanical framework (see [21] for the detailed discussion of differences between those approaches). In the current work we use ab initio local stress calculation technique first introduced in [26]. That technique has the advantage of overcoming so-called gauge-dependent problem [27, 28]. Calculations were performed using Open source package for Material eXplorer (OpenMX) [29], the detailed discussion of the implementation of atomic stress in that software package will be published elsewhere.

3. Results

3.1. Stress - strain

Shear strain of absolute values (0.5, 1, 2, 4, 8) was applied to each structure, obtained by performing the procedure described in 2.1. In order to capture the effect of shear modulus softening [6], under particular strain we analyzed two structures: affine one (obtained directly from initial structure by applying the strain) and optimized one (obtained after performing atomic positions optimization in affine structure). The stress - strain curve, which was achieved after averaging discussed in 2.3, is presented along with the curve reflecting optimized to affine stress ratio on the Fig.2.

Analysis of atomic stress lets us to point out that it is Zr atoms responsible for stress drop in the structures under shear strain. Stress was calculated for both affine and optimized structures. On the Fig.3 the distribution of difference in local stress on each atom can be seen for the structure under all studied strain values. It is clear that Zr atoms have mostly decreased pressure on them, while Cu atoms come to higher pressure after optimization of the affine structure. Summarized stress difference in case of 8% strain equals to 1.377 GPa and -3.305 GPa for Cu and Zr atoms correspondingly, which leads to -1.928 GPa stress drop for the whole structure (see Fig.2). According to our calculations, the stress distribution of that type holds for all strain values.
3.2. Properties of the structure

Before the direct explanation of why Zr subsystem provides the stress drop to the system, let us focus on the topological properties of structures under study. From the PDF shown on the Fig. 4 one can derive the cut-off distance of 3.85 Å, within which atoms can be referred to as first coordination sphere neighbors. Using that cut-off distance, the coordination number was calculated for each atom. Along with the Voronoi volume of atoms (see Fig. 5) it gives expected result of Zr atoms with bigger volume and therefore higher coordination number.

Charge distribution (Fig. 6) shows strong transfer of electrons from Zr to Cu atoms. It is worth mentioning that in order to determine the charge associated with each atom the volume according to Bader definition [30] was used. The Bader volume differs from Voronoi volume as can be seen from the inset of the Fig. 6 however that fact was already discussed (see for example [31]).
3.3. \textit{Cu} and \textit{Zr} subsystems interaction

In order to show the difference in the behavior of Cu and Zr subsystems under the strain, let us discuss 3-atoms angle change induced by the optimization of atoms positions in the affine structure, which turns it to the optimized structure. The most clear information can be obtained from such angle change for atoms of the same type in the structure under high strain, as presented on the Fig.7(a). For each atom we found closest neighbors of the same type as targeted atom. Next, for that group of atoms we calculated change of all unique 3-atoms angles with targeted atom being the vertex, and averaged it to get one value associated with each atom of the structure. Since some atoms have less then 3 same type first neighbors, the negative value of 3-atoms angle is assigned to them in order to avoid ambiguities. Taking only neighbors of the same type we can analyze separately Cu subsystem and Zr subsystem of atoms. However, augmenting that data with the number of Cu closest neighbors for each atom, which is shown on the Fig.7(b), one can see the interactions between the subsystems.

It can be seen on the Fig.7(a) that Cu subsystem is rearranged dramatically in the
optimization process, while Zr-Zr angles are changed only slightly. Also it is clear that a lot of Zr atoms have only few same type first neighbors, and moreover in general, each Zr atom has more atoms of Cu type as first neighbors, than of Zr type. The last proposition can be understood from the fact that Zr-Zr equilibrium distance is bigger than Cu-Cu (see corresponding PDFs on the Fig.4), which leads to Zr atoms being mostly pushed apart from each other, while Cu atoms tend to stay at closer distances.

Let us emphasize that local stress calculations gave as atom number 89 as the one with the biggest stress drop (see Fig.3). At the same time that atom has the biggest number of Cu neighbors. Summarizing, it can be stated that Cu subsystem is adjusting under the strain, but that adjustment serves to more stiff Zr subsystem. A lot of Zr atoms appears in the better geometrical environment after the optimization, and hence provide stress drop for the whole system.

4. Conclusion

To the best of our knowledge, it is the first time, when a metallic glass structure is studied under shear strain by means of ab initio calculations. Thorough simulations of Cu_{50}Zr_{50} glassy alloy under shear strain have been conducted. It was shown that Zr subsystem shows very stiff behavior, while providing high stress drop to the whole system. On the other hand, Cu subsystem undergoes severe rearrangement under the shear strain, surprisingly resulting in higher stress on Cu atoms.
Figure 7: (a) Average change of 3-atoms angle for atoms of the same type in the CuZr structure under 8% shear strain. (b) Number of Cu atoms within first coordination sphere of each atom in affine and optimized CuZr structure under 8% shear strain.

The evidence from our results points toward the atomic-level mechanism of shear modulus softening in CuZr metallic glass. Nevertheless, studies of more stoichiometries are needed to prove our hypothesis.

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