Molecular Dynamics simulations of Cu$_{64}$Zr$_{36}$ metallic glasses

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Abstract

This report covers the first year of a project where the structure of Cu$_{64}$Zr$_{36}$ metallic glasses is simulated by Molecular Dynamics. An amorphous sample is produced by quenching from the melt. The pair correlation functions of the liquid and the glass are calculated and compared for different temperatures. The topological short-range order is analyzed by the Voronoi tessellation method. The most prominent atomic arrangements in the glass are Cu-centered icosahedra. Subsequently, the sample was uniaxially compressed to investigate the mechanical deformation in metallic glasses. A stress-strain curve was measured, which shows stress drops in the plastic regime that might stem from shear-transformation zones. However, larger systems have to be investigated to observe shear-band formation, which is known to be present in the real material.

Introduction

Metallic glasses (MGs) are amorphous alloys with unique mechanical, electric, and magnetic properties. They are produced by rapid quenching from the melt. The critical cooling rate to avoid crystallization is on the order of $10^6$ K s$^{-1}$ for conventional binary metallic glasses (MGs) and $10^2$ K s$^{-1}$ for bulk metallic glasses (BMGs) [1]. Therefore, the critical casting thickness of MGs is limited to a few micrometers, while BMGs have a casting thickness larger than 1 mm. Usually BMG-forming systems contain more than three different elements with large differences in the atomic sizes. However, also binary Cu–Zr can be cast into a metallic glass with a thickness of 2 mm [2], which is exceptional for a binary system. The advantage of a binary system is that the structural description becomes more feasible, when compared to multi-component systems, so that it is better suited for structural investigations. The structure of metallic glasses is characterized by the absence of any long-range translational order. Only short- and medium-range order exist and can be observed by means of x-ray diffraction (XRD) or extended x-ray absorption fine structure (EXAFS). The actual
arrangement of the atoms, however, is difficult to determine by experimental techniques and thus computational methods such as Molecular Dynamics (MD) are employed. In fact, MD is not only capable of simulating the static structure of metallic glasses but can also be used to simulate dynamic properties, e.g. plastic deformation or relaxation. Plastic deformation in metallic glasses works fundamentally different than in crystals, where the strain is mostly carried by dislocations. The deformation in MGs is highly localized in so-called shear-bands, which have a thickness of several nanometers. In this study the structure of amorphous Cu$_{64}$Zr$_{36}$ is simulated by MD simulations. Initially a metallic glass is produced by quenching from the melt. The sample will then be mechanically deformed to investigate the structural origins of and changes during plastic deformation.

**Methods**

The MD simulations were carried out using the LAMMPS simulation package [3] and the embedded-atom potential provided by Mendelev et al. [4]. An amorphous Cu$_{64}$Zr$_{36}$ sample with a total number of 11'664 atoms was prepared in multiple steps. Starting from a cubic atomic arrangement, the sample was heated to 2000 K and equilibrated for 2 ns ($10^6$ time steps). Next, the sample was quenched to 50 K using a cooling rate of 0.1 and 0.01 K ps$^{-1}$, respectively. Slight changes in the pair correlation functions were observed so that we decided to continue with the slower cooling rate to obtain a more realistic simulation. The computation time when using 128 processors is about 0.005 s per time step, so that the entire simulation time (including the melting, equilibration and quenching) is of the order of days. Pair correlation functions were calculated at 2000 K, 1200 K, 800 K, 680 K, and 50 K after equilibration for 0.2 ns and averaging the data from 50 successive configurations taken with a time interval of 1 ps. The total and partial coordination numbers were calculated by counting the nearest-neighbor atoms. The radial cut-off value was defined as the radius where the pair correlation function has its first minimum beyond the nearest-neighbor peak. To study the topological short-range order, the Voronoi tessellation method was applied for the liquid alloy (2000 K) and the glass (50 K). A Voronoi polyhedron (VP) is assigned to every atom, so that every point inside the VP is closer to the central atom than to any other atom in the structure. Every VP has its own Voronoi index (VI) $<n_3 n_4 n_5 n_6>$, where $n_i$ is the number of $i$-edged faces of the VP. For example, the VI of an icosahedral atomic arrangement is $<0 0 12 0>$ as the corresponding VP is a dodecahedron. The frequency of different VI provides information on the most prominent structural patterns that are present.
After analyzing the static structure we studied plastic deformation of metallic glasses. The sample is uniaxially compressed in the z-direction with free movement in the x- and y-direction, a deformation rate of $2 \times 10^7$ s$^{-1}$, and periodic boundary conditions.

**Results and discussion**

The structure of Cu$_{64}$Zr$_{36}$ was studied at 2000 K, 1200 K, 800 K, 680 K, and 50 K to follow the evolution of the atomic arrangements during cooling. When plotting the volume per atom against the temperature (Fig. 1) a discontinuity is observed at approximately 720 K, which corresponds to the glass transition temperature $T_g$, where the undercooled liquid freezes and forms a metallic glass. The value is close to the experimental $T_g = 745$ K. The respective pair correlation functions are shown in figure 2. During cooling the height of the first peak of the pair correlation function increases while the full width at half maximum decreases. This indicates that the atomic neighbor-shells are defined better at lower temperatures, especially when comparing the glassy and the liquid state. In addition, the second peak is becoming more structured at lower temperatures hinting at increased topological order in the next nearest-neighbor shell. A better understanding of the actual atomic arrangements is provided by the Voronoi tessellation method: At 2000 K 0.2% of all copper-centered clusters are full icosahedra (FI) (Fig. 3a) with a VI of $<0 0 12 0>$ and 1.3% are distorted icosahedra (DI) (Fig. 3b) with a VI of $<0 2 8 2>$. After solidification the icosahedra are the most prominent clusters as their relative amount increases to 10.8 % FI and 7.1 % DI. This result agrees with earlier reports in the literature [5, 6].

In table 1 the partial and total coordination numbers are shown and compared to results from the literature for *ab initio* calculations [7] and Reverse Monte Carlo (RMC) simulations [8]. While the results from *ab initio* simulations are close to the results in this work, the coordination numbers from RMC simulations are different. This is not further surprising as the RMC method simply produces an atomic configuration that reproduces XRD and EXAFS data, without considering a physical potential.

The mechanical properties of metallic glasses are characterized by a high yield strength and low plasticity due to the absence of dislocations. In metallic glasses, plasticity is highly localized in thin shear-bands with a thickness of some nanometers. The sample in this work, however, is smaller than the typical size of a shear-band which therefore cannot be observed. Figure 4 shows the stress-strain curve recorded in compression with a deformation rate of $2 \times 10^7$ s$^{-1}$. The sample exhibits a yield strength of 3.5 GPa and an elastic strain of approximately 6%. The experimental values of Cu$_{64}$Zr$_{36}$ are ~2 GPa and ~2.2%, respectively.
When comparing these values one has to be aware of the much higher cooling rate in the simulation, which is 11 orders of magnitude faster than in the experiment. The stress drops in the plastic regime might be a result from local atomic rearrangements (shear transformation zones), which has to be checked.

**Conclusions and Outlook**

Amorphous Cu<sub>64</sub>Zr<sub>36</sub> was simulated by using MD. The change of the topological short-range order is seen in the pair correlation functions, which were calculated at different temperatures during cooling. The Voronoi tessellation method unveiled an increase of icosahedra during glass formation. In the second part uniaxial compression was applied on the sample and a stress-strain curve was measured. However, to observe shear-band formation a larger sample (> 1 million atoms) is required, which will be built by several replicas of the sample from this work. The deformed sample will then be analyzed locally to identify the differences in- and outside the shear-band region.

**Table 1**: Partial and total coordination numbers compared with the literature.

<table>
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<th>ab initio [7]</th>
<th>RMC [8]</th>
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<td>Cu-Cu</td>
<td>5.9</td>
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<tr>
<td>Cu-Zr</td>
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<td>4.6</td>
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<tr>
<td>Zr-Zr</td>
<td>4.8</td>
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<tr>
<td>Total</td>
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<td>13.1</td>
<td>13.2</td>
</tr>
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Figure 1: Volume per atom depending on temperature during cooling. At 720 K a discontinuity indicates the glass transition.

Figure 2: Total pair correlation function g(r) at different temperatures during cooling. With decreasing temperature the first peak narrows and becomes larger indicating a better defined nearest-neighbor position. Additional features appear in the second peak meaning that also the next nearest-neighbors are arranged more systematically.
Figure 3: (a) Full Cu$_6$Zr$_7$ icosahedron with a VI of $<0 0 1 2 0>$; (b) Distorted Cu$_8$Zr$_5$ icosahedron with a VI of $<0 2 8 2>$. Copper atoms are colored orange and zirconium olive. The bonds are only drawn for better 3-dimensional visibility and do not represent physical bonds.

Figure 4: Stress-strain curve in compression for a strain rate of $2 \times 10^7$ s$^{-1}$.