Mechanical and structure studies of Zr$_{50}$Cu$_{50}$ glass matrix composites during nano-indentation-a molecular dynamics study

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Abstract. In this paper we report molecular dynamics simulations of nano-indentation on Zr$_{50}$Cu$_{50}$ metallic glass matrix composite (14% crystalline volume fraction) at various strain rates. The objective of this paper is to investigate the effect of strain rate on the deformation behaviour and understand the deformation mechanism during deformation. Structural analysis during deformation is done by centro-symmetry parameter (CSP) studies. The load-displacement plots are drawn for the loading portion of indentation to analyze the deformation behaviour. It is found that strain rate has significant effect on the nature of the load-displacement plot. With increasing strain rate serrations decreased and flat load-displacement regime is observed with progress of indentation (~10 Å) at strain rate of $1 \times 10^{11}$ s$^{-1}$. This could be due to atoms getting less time to get rearranged themselves so as to bear further load. Also, the structure studies by CSP indicated that, at low strain rates ($2 \times 10^{10}$ s$^{-1}$ and $5 \times 10^{10}$ s$^{-1}$) there is significant plastic deformation of the crystallite as compared to that at high strain rate value of $1 \times 10^{11}$ s$^{-1}$ at a particular indentation depth. This indicates that there is load transfer from the glassy matrix to the crystallite much earlier at low strain rates. However, at indentation depths of 20 Å at all the strain rates amorphization of the crystallite is observed.

1. Introduction

Bulk metallic glasses (BMG) are used for structural applications because of distinctive mechanical properties compared to crystalline materials like higher strength (1.8 GPa), higher elastic strain (~2 %) good corrosion resistance, higher hardness [1-3]. But they exhibit limited plasticity in compression and negligible in tension (<0.5 %) [1, 4 and 5]. So, they become prone to catastrophic failure which bounds their use in limited functional area. There are several types of BMGs such as Cu-based, Zr-based, Ti based, Fe-based [6]. The most widely studied are Cu-based metallic glass as they have good glass forming ability, high thermal stability, high corrosion resistance and high strength [6]. The deformation mechanism in BMGs is different from that of crystalline materials due to the absence of dislocations. The deformation studies revealed that at low strain rate, BMGs fail in discrete manner by shear banding which results in brittle failure while this deformation becomes continuous at high strain rates and not in discrete manner. This is due to the formation of a single shear band at low strain rate which is not able to bear sudden high strain values so multiple shear bands are formed at high strain rates [7]. To improve the ductility, BMG composites were synthesized. It was found that there was significant increase in the plastic strain due to the obstruction of the rapid propagation of shear bands in the presence of crystallites [5, 8]. Several deformation studies were done on BMG reinforced with
crystalline particulates [2, 9]. It was found that, this reinforcement changed their mechanical properties like fracture toughness and ductility by formation of multiple shear bands. Addition of Nb to Zr_{57}Nb_{2}Al_{10}Cu_{15.4}Ni_{12.6} BMG to form composite increased its toughness [2]. Wang et al. [10] did experiments to show that the addition of Nb to Zr-Ti-Cu-Ni-Be metallic glass system resulted in increase of ductility due to formation of crystalline phases. The deformation mechanism in glasses is different to that of crystalline materials due to the disordered structure. There are several proposed deformation mechanism theories, such as STZ (shear transformation zone), shear band theory and free volume theory. As proposed by Argon [11] STZ is the fundamental unit of plastic deformation of metallic glasses similar to dislocation in crystalline materials. Further, STZ’s are local cluster of atoms of few nanometres that rearrange by the application of shear stress. This involves displacement of atoms, their inelastic reconfiguration and redistribution of free volume in these atomic clusters. A different theory for deformation behaviour in metallic glasses proposed by Spaepen [12] was based on free volume creation by stress and its destruction by diffusion.

In order to reveal the deformation behaviour of metallic glasses at the atomic level, several atomistic simulations have been done by shear, indentation, tensile and compression [13-16]. Most of the simulation studies are done by tensile or compression as it is easier to model. However, nano-indentation studies are seldom reported. The nano-indentation techniques employed were useful to detect sub-nanometre disturbances connected with “plasticity” phenomenon such as dislocation nucleation in crystalline materials and shear band localization and propagation in metallic glasses [17]. In the MD deformation indentation studies of Qiu et al., [18] on Cu_{50}Zr_{50} metallic glass substrate at different loading speed and temperature it was shown that, with increase of loading rate, the force required for indentation also increases but decreases with increase in temperature. Further, Liu et al. [19] did nano-indentation simulation study of Zr-based metallic glass sample (Zr_{55}Cu_{30}Ni_{10}Al_{5} and Zr_{60.2}Cu_{12}Ni_{11}Al_{1.3}). In these studies serrated plastic flow was observed in the load-displacement plots and found to be dependent on loading rate. Pang et al. [20] did experiment on binary MG thin film Cu_{49.2}Zr_{50.7} grown on Si substrate. It was shown that plasticity was delayed at high loading rate. Wu et al. [21] did nano-indentation experimental study of Cu_{52}Zr_{37}Ti_{8}In_{3} BMG and found that Young’s modulus and hardness both decrease with increase in depth of indentation. However, seldom nano-indentation studies have been reported on BMG composites.

The mechanical properties of amorphous metals or metallic glasses are affected by addition of nano-crystallitles and depend on crystal particle size, crystal volume fraction, strain rate of indentation, temperature of working and the amorphous-crystal phase interaction strength [22]. In the present investigation, the deformation behaviour of Zr_{50}Cu_{50} based glass matrix composites (GMC) and structural changes during deformation have been studied using nano-indentation technique at different strain rates (2 × 10^{10} s^{-1}, 5 × 10^{10} s^{-1} and 1 × 10^{11} s^{-1}) at room temperature. Since modelling of binary amorphous alloy is easier than alloys containing more than two alloys and also it reveals the properties of amorphous alloys so Zr_{50}Cu_{50} system was selected.

2. Molecular dynamics (MD) simulation procedure

Zr_{50}Cu_{50} model metallic glass matrix composite containing 14 % crystallite by volume was prepared by simulated melting and quenching. The simulation box size is of 100 Å × 100 Å × 100 Å dimension comprising of 87,808 atoms. Here, crystallites are arranged in FCC crystal structure. The equilibration of model was done at minimum energy configuration at a temperature of 300 K. Sample was relaxed under NPT (constant pressure and temperature) ensemble. The initial sample was heated from 300 K to 2300 K for 20 ps, allowing solid to melt and then held at 2300K for 100 ps. After that the sample was quenched from 2300K to 300K for 200 ps corresponding to cooling rate of 10^{13} K/s. The pressure was maintained at 0 bar during whole process. Nano-indentation was carried out on the sample with an indenter having a spherical tip (diameter 40Å) up to a depth of 20Å along Y-direction. The MD simulation of nano-indentation was employed under NVT (constant temperature and constant volume) ensemble. The bottom part of sample was kept fixed to prevent the substrate from moving in the direction of indentation during the whole simulation. The size of substrate was 100 Å × 20 Å × 100 Å.
Periodic boundary condition was applied in non-loading directions i.e., along X-axis and Z-axis. MD simulation of nano-indentation was carried out on glass matrix composite (GMC) to study its effect on the deformation behaviour. The strain rate used was $2 \times 10^{10}$ s$^{-1}$, $5 \times 10^{10}$ s$^{-1}$, and $1 \times 10^{11}$ s$^{-1}$. The simulation of nano-indentation comprised of indentation and equilibrium stages. In equilibrium stage the indenter was kept at a distance of 3 Å from sample in order to avoid long range attractive force between them. In the second stage the indenter moved downward to 20 Å inside the sample at above mentioned strain rates. The motion of each atom was governed by Newton’s second law of motion. Newton’s law of motion was integrated by velocity-Verlet algorithm with a time-step of 0.002 ps. Load-displacement curves were drawn for sample at various strain rates to study the nature of the curve. The EAM (embedded atom method) potential was used to describe the interaction between atoms. The total energy of an atom $E_i$ is given by Mendelev et al. [23] as

$$E_i = F_\alpha \left( \sum_{j \neq i} \rho \beta(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\bar{\alpha}}(r_{ij})$$

Where, embedding energy $F_\alpha$ is a function of atom’s electron density, is a pair potential interaction, and are the element types of atoms i and j. It is a widely used potential for studying the properties of materials [16, 18, 24-26]. All the simulations are carried out on LAMMPS platform which is a widely used open source code [27].

3. Results and Discussions

Figure 1 shows the atomic positions snap shot of Zr$_{50}$Cu$_{50}$ metallic glass composite in full (figure 1a) and sliced view (figure 1b). Spherical crystal (blue coloured) of 32 Å radius is embedded at the centre occupying 14 % volume.

![Figure 1: Atomic position snap shots of the Zr$_{50}$Cu$_{50}$ metallic glass composite: a) complete simulation box (red coloured atoms: Zr; green coloured atoms: Cu; b) sliced box revealing the central crystallite position (the atoms are coloured based on the centro-symmetry parameter values (blue colour: perfect crystal)).](image)

Figure 2 shows the load applied on the indenter and the depth of indentation in the Zr$_{50}$Cu$_{50}$ metallic glass composite sample at different strain rates of $2 \times 10^{10}$ s$^{-1}$, $5 \times 10^{10}$ s$^{-1}$, $1 \times 10^{11}$ s$^{-1}$. All the curves show linear elastic behaviour and non-linear plastic behaviour. Elastic behaviour is shown up to first load drop in the curve. The vertical force on the indenter increases elastically from zero according to Hertz theory before the beginning of plastic deformation [28]. The expression for the load is given by the following equation.
Where, $P$ is load, $R$ is the reduced elastic constant and $a$ is half of the projected contacted length. $L_y$ is the length of the simulation box in the $y$-direction. $E^*$ is the reduced Young’s modulus in plain strain conditions. The curve changes its slope after the first load drop indicating plastic deformation occurring with further loading. The first load drop or yield point appears at lower indenter displacement with increase in strain rate indicating plastic deformation at early stage of deformation. These plastic deformations are indicated by “pop ins” or serrations [17] in the curve which are more pronounced (of larger size) at lower strain rates of $2 \times 10^{10}$ s$^{-1}$ and $5 \times 10^{10}$ s$^{-1}$ and decreases with increase of strain rate to $1 \times 10^{11}$ s$^{-1}$. This is so because at low strain rates atoms get enough time to rearrange and bear further load, so there are more fluctuations in the load value leading to more pronounced serrated curve. Number of rearranged atoms is also more which is an indication of high degree of plastic deformation. Whereas, at high strain rate atoms get very less time to rearrange and so load drops are less and so number of serrations are less. Number of rearranged atoms is also less causing less degree of plastic deformation. This phenomenon is coherent with the simulation result presented by Jiang et al. [13]. The load drops are irregularly spaced in all curves which may be due to short range order structure of GMC. We can observe that the amplitude of serrations decrease with increasing strain rate as shown in figure 2(a) to (c). This is so because atoms do not get enough time to rearrange and bear further load at high strain rates but as amorphization of atoms is delayed with increase in strain rate so the maximum load value increases gradually with rise of strain rate value as shown in Table 1. So, with increase in indenter displacement even after the yield point, the load on the indenter also increases.

\[ P = \frac{\pi a^2 E^*}{4R} L_y \]
Table 1. Mechanical properties of Zr$_{50}$Cu$_{50}$ metallic glass composite containing at different strain rates

| Strain rate (s$^{-1}$) | Yield point (nN) | Maximum load value (nN) |
|------------------------|------------------|------------------------|
| 2 × 10$^{10}$          | 49               | 127                    |
| 5 × 10$^{10}$          | 73               | 149                    |
| 1 × 10$^{11}$          | 132              | 178                    |

Figure 3. Atomic snap shots of the Zr$_{50}$Cu$_{50}$ metallic glass composite during nano-indentation at different depth of indentation a) initial; b) 0.16 Å; c) 0.36 Å; d) 0.52 Å; e) 12 Å; f) 20 Å and at different strain rates: 2 × 10$^{10}$ s$^{-1}$ (Fig. 3.1); 5 × 10$^{10}$ s$^{-1}$ (Fig. 3.2); 1 × 10$^{11}$ s$^{-1}$ (Fig. 3.3).

In order to reveal the structural details during deformation, CSP studies are done. Figure 3 shows the atomic snap shots of Zr$_{50}$Cu$_{50}$ metallic glass composite at different depths of indentation during nano-indentation along y-direction and at different strain rates i.e., 2 × 10$^{10}$ s$^{-1}$; 5 × 10$^{10}$ s$^{-1}$ and 1 × 10$^{11}$ s$^{-1}$. The centro-symmetry parameter (CSP) is used for analysis of the structural changes during indentation. The colour coding is done according to the intensity of defects. CSP value of zero indicates no defects while CSP value of twelve indicates surface and stacking fault defects. The red
and green atoms surrounding the blue circular region (crystallite) is Zr\textsubscript{50}Cu\textsubscript{50} metallic glass. The crystallite initially is free of defects (figure 3.1a, figure 3.2a, and figure 3.3a), but with progress of indentation plastic deformation of the crystallite occurs at all strain rates along with that of glassy matrix. It can also be seen that the crystallite becomes amorphous at the indenter displacement of 20 Å at all strain rates. It is well known that the deformation mechanism in glass is different from that of crystals. At indenter displacement of 0.52 Å (figure 3.1d) in the strain rate of $2 \times 10^{10}$ s\textsuperscript{-1} (figure 3.1) more defects (colour index) are introduced in the crystallite as compared with the other two strain rates (figure 3.2d and figure 3.3d) resulting in flat load-displacement plot in that regime. This clearly indicates that at higher strain rates, deformation of the glass occurs rather than crystallite. In the sense there is no load transfer from the glassy phase to the crystallite phase at higher strain rates.

4. Conclusions
1. Strain rate has significant effect on the load-displacement plot. With increasing strain rate yielding load increases.
2. With increasing strain rate serrations decrease, indicating that atoms get sufficient time for atomic rearrangements at lower strain rates and contribution for plastic deformation.
3. Structural studies by centro-symmetry parameter showed that at strain rate of $2 \times 10^{10}$ s\textsuperscript{-1}, plastic deformation of the crystallite occurs even at smaller indenter displacements as compared to the $1 \times 10^{11}$ s\textsuperscript{-1} strain rate.

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