Enhancement of Plasticity of Highly Density-Fluctuated Cu-Zr Amorphous Alloy

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This study explores the plastic deformability of highly density-fluctuated states due to the different thermal quenching process of the binary amorphous metals, Zr67Cu33, with embedded nanocrystals, Zr2Cu. To know the effect of local structural fluctuation, we prepare 5 computational models with Zr2Cu-nanocrystals that undergo rapid heat up and cool down. The region of nanocrystals is corresponding to the dense area because the intrinsic density of crystal is greater than that of amorphous structure. Due to the distribution of nanocrystals, the artificially constructed models have highly density-fluctuated structures (called “structural-inhomogeneity”). Strain localization during plastic deformation is much retarded at structural-inhomogeneous model in tensile loading. We found that structural-inhomogeneity promotes more homogeneous deformation (call “deformable-homogeneity”, that is, retarded strain localization) even in globally recognized elastic region, while structural-homogeneity (almost close to pure amorphous structure) makes catastrophic inhomogeneous deformation (catastrophic shear band).


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1. Introduction

The deformation of metallic glasses is mainly driven by inhomogeneous deformation, a kind of strain localization called shear band. Except at temperature sufficiently high to allow homogeneous deformation, these strain localizations are directly related to strength and fragility of metallic glasses. Unstable and abrupt failure due to just a few shear bands is usually found on uniaxial tensile or bending test.1–10 It is important to understand the mechanism of shear band formation since abrupt failure related to fragility prevents amorphous materials from being used in industrial applications.

In order to avoid the fragility, a lot of experimental researches have been investigated up to date on amorphous composite materials containing nanocrystals.5,8–10 It is also reported that ductility or plastic deformation can be improved by crystalline phases in metallic glasses up to 35%, due to multiple shear bands promoted by crystalline phases.5–10 Consequently, structural-inhomogeneity induced by nanocrystals makes deformable-homogeneity (retarded strain localization by multiple shear bands), but, structural-homogeneity induced by pure amorphous structure makes catastrophic-inhomogeneity (abrupt strain localization by just a few shear bands). However, metallurgical processing to control the morphological conformation of such a second phase still has a lot of a difficulty. On the other hand, some experiments on the successful synthesis of bigger-sized bulk metallic glasses (BMG) reports the unintended but self-generated density fluctuation in the BMG11 might strongly affect to the plastic deformation.12 Therefore, it is much interested in realizing the variation of fragility at amorphous materials with highly density-fluctuated structure. This work explores the plastic deformability of highly density-fluctuated states due to the different thermal quenching process of the binary amorphous metals, Zr67Cu33, with embedded nanocrystals, Zr2Cu using molecular dynamics (MD) simulations under plane stress condition.13–19 The region of nanocrystals is corresponding to the dense area because the intrinsic density of crystal is greater than that of amorphous structure. Due to the distribution of these nanocrystals, models have highly density-fluctuated structures. This choice is motivated by a number of recent publications for strain localization using MD simulation.14–19 These researches find the mechanism of shear band formation is related with the quasi-crystal like short range order, the mass density of pure amorphous materials and the number of nanocrystals.

2. Computational Model Setup

To make computational model, we choose about 100,000-atoms Zr67Cu33 system with pure amorphous structure as an initial amorphous structure at the first step. The fully relaxed structure for 200 ps has the size of about 30nm × 30nm × 22nm. Besides, Zr2Cu crystals with perfect C11b structure (one of body-centered cubic structures) found easily in the experiment of binary system and with size of about 1.3nm × 1.3nm × 22nm are prepared as an initial crystal structure.20 The interatomic potentials employed here are much simple two-body form, but they can realize both amorphous and crystal structures, as described below.21 Holes with almost same size of crystals are carved in the amorphous materials, and then the crystals are inserted into the amorphous structure. As shown in Fig. 1, 196 nanocrystals (14 rows and 14 columns) are evenly distributed on amorphous basis. The initial volume fraction of nanocrystals is around 17%, based on the number of atoms with crystal structure. The mixed structure is relaxed for 200 ps at 300K again before receiving heat treatment. As the case now stands without any heat treatment, we get the as-relaxed model. Table 1 shows elastic constants, lattice constant and density22,23 for each structure, amorphous structure and crystal
structure measured by conjugate gradient method. As can be expected, C11 is equal to C33 at amorphous structure because of homogeneity of structure. To the best of our knowledge, there is no way to generate crystals by itself on binary amorphous structure during cooling down on MD simulation. It is believed that the atoms cannot have enough relaxation time to go to globally stable position, not locally stable position, on MD simulation because of computational time limitation. In contrast, the atomic crystal of Zr\textsubscript{2}Cu with C11\textsubscript{b} lattice structure has successfully been realized using the same potential employed here. The preliminary simulation on heating-cooling process of this crystal gives the melting temperature of 2400 K during heating and the glass transition temperature of 950 K during cooling-down and thus the range between two is thought to be superliquid state in the present model, as shown in Fig. 2. Based on the characterizations of the present computational models, the mixed structures with inserted nanocrystals are relaxed at below melting temperature.

To adjust the several density-fluctuated states from the artificially made-amorphous composites, the as-relaxed model is quenched at quenching rate of \(2 \times 10^{12} \text{ K/s}\) from 600 K (Model 1), 1000 K (Model 2), 1200 K (Model 3), 1400 K (Model 4) and 1800 K (Model 5), which range from the superliquid state to below melting temperature, as mentioned above. After quenching process, the temperature keeps a constant 300 K for 400 ps or more. At this moment, the volume fractions of atoms with BCC structures are changed from 2% to 17% of entire atoms depending on quenching temperature. Consequently, all models come from the same model, but have different density fluctuation with crystallites-like local configuration.\(^\text{24}\) We call them as-prepared models.

To make shear band easily during the deformation process, we employ molecular dynamics study using modified Lennard-Jones potential under plane stress condition.\(^\text{13,25,26}\) It means that \text{z}-coordination of each atom is fixed in 3-dimensional model, allowing the change of whole atomic cell in \text{z}-direction so as to make stress in \text{z}-direction zero. However, we switch the model to the 3 dimension only when measuring the atomic strain using the developed program.\(^\text{25}\) So far it is impossible to make multi-shear bands in full 3-dimensional model with full periodic boundary condition, except the samples with nano-order thickness.\(^\text{18}\) The length of \text{z}-direction is 22 nm (the thickness of pure amorphous model) in this paper unless there is a special mention. With these conditions, the models are subject to uniaxial tension using high strain rate, \(5 \times 10^9 \text{ s}^{-1}\), because of computing time. The pressure is also controlled constantly by changing the size of whole model.

To quantify the strain localization, atomic strain based on the volume for each atom is measured using the definition suggested by Mott and Argon.\(^\text{27}\) Then, deviatoric distortion is calculated using the measured atomic strain. In order to represent the deviatoric distortion, we express the octahedral strain as follows:

![Fig. 1 Schematic of mixed models where \(L\) is about 30 nm, \(d\) is 1.3 nm. The total number of inserted crystals is 196. At each column and row, 14 crystals are positioned.](image)

![Table 1 Mechanical properties of amorphous and crystal structure.](table)

<table>
<thead>
<tr>
<th>Model</th>
<th>Structure</th>
<th>(C_{11}) (GPa)</th>
<th>(C_{33}) (GPa)</th>
<th>(C_{12}) (GPa)</th>
<th>Density (kg/m(^3))</th>
<th>Lattice Constant, (nm,lateral)</th>
<th>Lattice Constant, (nm,vertical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr\textsubscript{67}Cu\textsubscript{33}</td>
<td>Amorphous</td>
<td>168</td>
<td>168</td>
<td>55</td>
<td>6720</td>
<td>0.324</td>
<td>1.114</td>
</tr>
<tr>
<td>Zr\textsubscript{2}Cu Crystal (MD)</td>
<td>Crystal (Ab-initio)</td>
<td>146</td>
<td>126</td>
<td>57</td>
<td>6920</td>
<td>0.321</td>
<td>1.122</td>
</tr>
<tr>
<td>Zr\textsubscript{2}Cu Crystal (Experiment)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.322</td>
<td>1.118</td>
</tr>
</tbody>
</table>

![Fig. 2 Relationship between whole volume of the model and temperature. Melting temperature of Zr\textsubscript{2}Cu and glass transition temperature of Zr\textsubscript{67}Cu\textsubscript{33} are around 2400 K and 950 K, respectively.](image)
\[ \gamma_{ij}^2 = \frac{1}{3} \text{Tr} \left( \varepsilon_{ij} - \frac{1}{3} \varepsilon_V \delta_{ij} \right) \]  

where \( \varepsilon_V \) is the volumetric strain. This definition and more detail for atomic tensor can be found in the reference. 27)

3. Results and Discussion

Figure 3 shows atomic configurations of as-prepared state for all models. Each model has different quenched temperature. Due to the temperature, each model has different atomic structure. As seen in Fig. 3, Models 1 and 2 still remains a lot of crystal structures while models 4 and 5 seem not to show any crystal structures. Model 3 also has many crystals on the observed surface, but the number of crystal is apparently less than that of Model 1 or 2. Although model 3 seems to be at transient state, all properties already go to steady state. In addition, all models are fully relaxed for a long time after quenching process as shown in Fig. 4 and each model reaches the quasi-stable state with their own structure. Temperature and Time curves are represented in the box figure.

To quantify the amount of crystal-based local structure, the percentage of atoms with BCC structures are measured by weighted Voronoi analysis considering the size of atoms. 28) All of atoms including amorphous part and crystal parts are analyzed. As mentioned above, the inserted crystal structure, C11b, is a kind of BCC structure. The BCC structures are considered as Voronoi polyhedron only with (04460) or (06080) denoted by Schläfli notation. Some atoms with (04460) or (06080) Voronoi polyhedron apparently have crystal structure, but others are not. However, most of them come from the crystal structure. The percentage of atoms with BCC structure and the averaged density of the whole system are shown in Fig. 5. Each point is corresponding to each model. For examples, the leftmost points are model 1 with 600K quenched temperature. As seen in the figure,
density curve shape is identical to that of the percentage of atoms with BCC, because the density of crystal is larger than that of amorphous in Table 1. Models 1 (600 K) and 2 (1000 K) have high BCC percentage and high density, 17% and 6737 kg/m$^3$ as expected. However, models 4 and 5 have relatively low BCC percentage and density below 2% and 6720 kg/m$^3$, respectively, which densities are much closer to that of pure amorphous structure (6719 kg/m$^3$) made by quenching over melting temperature. And we also check the Radial Distribution Functions of all model have split second peak. It is noteworthy to mention that model 3 have 10% crystal percentage. Namely, model 3 is located between fully mixed structure and pure amorphous structure. Due to this transient feature, model 3 has been relaxed for longer time (3 times than others). However, there is no noticeable difference for all properties. It also should be mentioned that the percentage difference between model 1 and model 5 reaches to 15%. This difference suggests that model 1 has highly density fluctuated structure, i.e. more inhomogeneous structure (called “structurally-inhomogeneous”), but model 5 has rather homogeneous structure with less density fluctuation than model 1 (called “structurally-homogeneous”).

Like BCC structure, the percentage of atoms with icosahedral structure is also measured by weighted Voronoi analysis. Figure 6 depicts the icosahedral structure percentage of each model. Models 1 and 2 with totally mixed structure show just 1% icosahedron percentage. Models 4 and 5 with pure amorphous structure show greater percentage than models 1 and 2. The percentage of icosahedron of model 3 is located at middle like that of BCC structure. The percentage difference of icosahedron is around just 1.5%. This value is relatively small compared to the percentage difference of BCC structure, 15%. As the quenched temperature increases, the structure goes to the pure amorphous structure where Zr$_{67}$Cu$_{33}$ made by quenching over melting temperature is drawn at 2.6%.

Uniaxial tensile loading is applied to all models, until strain reaches to 0.25. Figure 7 shows stress-strain curves for the models with different quenched temperature. During deformation, all curves reach the maximum then suddenly drop. The sudden drops are caused by the formation of shear band, as depicted in Fig. 7. Insets of Fig. 7 show typical configuration of shear bands at model 5. It is already found that the cooling rate of samples and the deformation strain rate also affect to the maximum stress and the overall curve shape. In Fig. 7, the maximum stress and the gradient of curve corresponding to the elastic modulus are apparently decreased as decreasing the quenched temperature, and the corresponding strain to maximum stress is increased as the percentage of BCC structure increases, that is, the plastic deformability is more improved. It means density fluctuation by BCC crystal structure makes strain localization retarded. In other words, the structural-inhomogeneity easily induces the homogeneous deformation (called “deformable-homogeneity”, that is, retarded strain localization). It could be possible that atoms in the structural-inhomogeneity can find
more stable position easily during deformation because the density fluctuation, i.e. free volume fluctuation, makes atoms move easily even at very low strain. Consequently, resistance for deformation in the structural-inhomogeneity (for example, Models 1 and 2) will be achieved softly because the stored strain energy by the external work is already dissipated by atomic moving. However, it is harder for atoms to find big enough free volume to move in the structural-homogeneity (for example, Models 4 and 5). So, for the atoms to drop into the local minima will be limited during the deformation. Consequently, the structural-homogeneity will be able to keep the high energy state and strongly resist for deformation. Then, at the state with higher stress and smaller strain, it will be deformed abruptly, which means severe strain localization.

In order to make clear of the above-mentioned scenario, statistical standard deviations of atomic volumetric strain and atomic deviatoric strain calculated by atomic strain tensor\(^26\) are shown in Fig. 8. In the sense of deformation, inhomogeneous deformation produces the large deviation of strain. Especially, standard deviation of atomic volumetric strain will give how much the models are inhomogenized, namely, strain localization. Even at very low strain state (globally recognized elastic region) such as 0.05 strain, the structural-inhomogeneous models (models 1 of 600 K and 2 of 1000 K) have less deviation in both strain, atomic deviatoric strain and atomic volumetric strain, than the structural-homogeneous models (models 4 of 1400 K and 5 of 1800 K). At finite strain of 0.1, the trend becomes clearer. The structural-homogeneous model has large standard deviation. It makes sense because it has already reported in some paper\(^7\) that the amorphous structures with the larger number of crystals (structural-inhomogeneity) have richer multiple shear bands.

Although multiple shear bands are also a kind of strain localization, we express deformation with multiple shear bands as homogeneous deformation because much multiplication of shear bands globally results in the homogeneous deformation. Namely, multiple shear bands can avoid the catastrophic localized deformation by just a few shear bands, and it makes smaller standard deviation of volumetric strain, for example, models 1 (600 K) and 2 (1000 K) indicating the homogenized deformation state.

4. Conclusion

We perform molecular dynamics simulation for binary amorphous materials with highly density fluctuated structure induced by inserted nanocrystal structures. In tensile loading, the percentage of crystal structures makes strain localization retarded. We also found that structural-inhomogeneity induced by density-fluctuation makes deformable-homogeneity which means less deviation of atomic volumetric strain and deviatoric strain, while structural-homogeneity induced by pure amorphous structure promotes catastrophic-inhomogeneity which means more deviation of atomic volumetric strain even in elastic region.

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All models used in this study are relaxed at below melting temperature. Some part of placed crystals already goes back to pure amorphous structures, but others still remain in density fluctuation structure even at below melting temperature. It means that there are no clear boundaries discriminating the crystallites and density fluctuation which is not a crystalline phase. Therefore, as mentioned in the main text, we treat density fluctuation and crystallites in an identical manner.

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