A computational analysis of the deformation mechanisms of a nanocrystal–metallic glass composite

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Received 9 July 2007; received in revised form 24 September 2007; accepted 1 November 2007
Available online 26 December 2007

Abstract

Simulations of a monatomic model amorphous matrix embedded with approximately 37% of a body-centered cubic phase demonstrate mechanisms by which nanocrystallites can alter the mechanical response of metallic glass. Three effects affect the resulting ductility: (i) the presence of weak amorphous–crystalline interfaces, (ii) the fraction of nanocrystallites oriented to prevent twinning relative to the loading stress, and (iii) the shear-induced growth and dissolution of the nanocrystallites when they are impinged by shear bands. While the first effect dominates in these simulations due to system size limitations, the third effect appears to be crucial for understanding the ductility of experimental samples. These simulations indicate that shear-induced growth of existing nanocrystallites, rather than nucleation of new crystalline regions, may account for the observed enhancement in ductility.

Keywords: Molecular dynamics; Metallic glass; Interface; Nanocrystal; Composite

1. Introduction

Bulk metallic glass (BMG) has been of great interest in recent years because of its unique combination of excellent mechanical properties and processing abilities [1]. One of the major drawbacks for monolithic BMG materials is limited ductility due to strain localization phenomena. Except for a few recent reports [2], the most popular method for enhancing the ductility of the BMG samples has been to introduce a secondary crystalline or quasicrystalline phase, either via nucleation [3–15] or by introducing second-phase particles directly [16]. The composite material usually exhibits some degree of strain hardening, significantly higher impact resistance and fracture toughness. For micrometer-sized inclusions, the plastic deformation initiates in the ductile crystalline phase and further deformation localizes within the crystalline phase. The deformation of the crystalline phase is mainly mediated by dislocations, and this is thought to account for the strain-hardening behavior. For nanometer-sized inclusions, dislocations become energetically unfavorable and the plastic deformation initiates at the crystalline–amorphous interfaces with further deformation occurring mainly within the amorphous phase. In these materials, the specific mechanism of strain-hardening is not fully understood. In addition, precipitation of nanocrystals has been observed in bending [17] and nanoindentation tests [18] on BMG samples. Such nanocrystallization appears to arise as the result of enhanced mass transport assisted by plastic deformation [19]. Recently, it has been proposed that the restraint of shear band propagation by dynamically precipitated nanocrystals is responsible for the ductile behavior of bulk Zr-based metallic glass [20,21]. Here we argue that even in the absence of the nucleation of new nanocrystals, the growth of existing nanocrystals facilitated by the plastic deformation may play a crucial role in enhancing the ductility of these nanocrystal–amorphous matrix composites.

We simulate uniaxial compression of a monatomic model amorphous system embedded with body-centered...
cubic (bcc) crystallites on the nanometer scale. We focus on identifying the location of the plastic deformation, the deformation mechanism of the crystallites and the interaction between the shear band and the crystalline inclusions. We have observed that, in contrast to monolithic glassy samples where a single shear band normally dominates, multiple shear bands appear in the composite samples. The plastic deformation initiates at the interfaces between nanocrystallites and the glassy phase due to the high potential energy and stress concentration at these interfaces. Furthermore, these simulations demonstrate that the growth of the nanocrystallites correlates with the shear band activity.

2. Model of atomic interactions

We consider the Dzugutov potential (DZ) as a model monatomic glass-forming system. This system is ideal for studying nanocrystal–amorphous composites because it is capable of precipitating nanocrystallites under compression. The DZ potential is described by the function

\[ U(r) = A(r^m + B) \exp \left( \frac{c}{r-a} \right) \Theta(a-r) + B \times \exp \left( \frac{d}{r-b} \right) \Theta(b-r). \]  

(1)

The parameters \( m, A, B, a, b, c \) and \( d \) are chosen as described in Ref. [22] and \( \Theta \) represents the Heaviside step function which enforces the short-range nature of each of the terms. Physical quantities are conveniently measured in internal units: \( \sigma \), a length scale approximately proportional to 88.5% of the bond length, and \( \varepsilon \), an energy scale approximately proportional to 1.72 times the binary interaction energy [22]. Thus it is easy to compare DZ system to the widely used Lennard–Jones system. The internal time unit is \( t_0 = \sqrt{m_0/\varepsilon} \) with a particle mass \( m_0 \). This potential features a maximum near the distance at which neighboring atoms would reside in order to form face-centered cubic (fcc), bcc or hcp crystals. Dodecagonal quasicrystals or Frank–Kasper crystals can be formed if the cooling rate is low [23], but at higher cooling rates, glasses are formed. The mode coupling temperature of this system \( T_{\text{MCT}} = 0.4 \varepsilon/k \), which sets an upper bound for the glass transition temperature [24]. For a typical glass-forming material, \( t_0 = 1 \) ps, \( \sigma \approx 0.3 \) nm and \( T_{\text{MCT}} \approx 1000 \) K. These assumptions will be used to express our result in conventional SI units.

3. Sample preparation

To prepare composite samples we begin with well-equilibrated liquids and systematically reduce temperature and pressure at constant rates to induce vitrification [25]. At the intermediate stage when the temperature is below the glass transition temperature and the pressure is non-zero, bcc crystallites can precipitate because the bcc phase is energetically favored [26]. Although precipitation from the melt, i.e. an in situ composite, can be produced experimentally as in Ref. [10], composites do not reliably form in these small simulated systems during the finite simulation time. Among 41 different quenching simulations using various quenching rates, only three systems contained bcc crystallites in the final state. To avoid this problem, we introduce bcc crystallite seeds into the glassy samples as in [27], analogous to ex situ composite preparation, so as to control the orientation, size and the spatial distribution of the BCC precipitates. The system is simulated in a slab geometry to maximize two of the three dimensions resulting in a system \( 21 \times 33 \times 5 \) nm\(^3\) containing about 112,000 atoms.

Sample preparation involves quenching well-equilibrated liquids from temperature 2500 K and pressure 7.81 GPa to a glassy state at temperature 800 K and pressure 2.37 GPa over a period of 5.25 ns. A bcc slab sample is prepared with the same temperature, pressure and length in the Z-direction as the amorphous sample. Approximately 30 through-thickness non-overlapping holes with a random radius between 1.5 and 2.1 nm are distributed randomly on the X–Y plane of the amorphous sample. Circular disks of matching size are then cut from the bcc crystal to fill those holes. Due to the periodic boundary conditions in the Z-direction, the crystalline inclusions are infinite in the thickness direction so that they are essentially crystalline nanofibers. To lower the potential energy of the crystalline–amorphous interfaces, the system is relaxed in an NVT ensemble for 0.1 ns with the atoms in the bcc nanocrystals fixed. The whole system is then relaxed for another 0.1 ns before quenching to 75 K and zero pressure in 0.3 ns. The final composite system contains about 37% bcc crystallites in terms of atomic weight.

Each sample thus prepared can be directly compared to the ones previously obtained via precipitation from melt. Fig. 1 shows the potential energy distribution for those two cases. The average potential energy profiles across the interface between the glass and the crystallite are measured for both cases. As shown in Fig. 1c the profiles overlap, indicating that the nanocrystallite–amorphous interfaces in our ex situ samples are identical to those in the in situ composite.

In previous simulation studies we have shown that the quenching rate of a monolithic glassy sample is crucial in determining its mechanical response including the degree of strain localization [25,28]. Here we investigate the effect of crystallite inclusions when introduced into a glassy phase which is prone to strain localization. Therefore, the quenching rate used here is low enough to exhibit strain localization at our lowest loading rates (NB: the glass matrix is very close to DZ-4 sample in Ref. [25] in terms of average potential energy) but high enough to avoid excessive crystal growth.

All bcc crystallites have their <011> directions aligned along the Z-direction of the simulation box while the in-plane orientation of the bcc crystal can be controlled during the seeding process. For nanoscale crystalline inclu-
twinning is the primary deformation mechanism \cite{29,30}. The twinning plane for typical bcc crystals is \( \{211\} \) and the twinning direction is \( \langle 111 \rangle \). Therefore, three types of composites are prepared: (1) composites with random orientation, which are denoted here as R composites; (2) composites in which the \( \langle 100 \rangle \) direction is set randomly within \( \pm 45^\circ \) of the compressive loading direction to suppress twinning, denoted here as N composites; (3) composites in which the \( \langle 011 \rangle \) direction is set randomly within \( \pm 45^\circ \) of the compressive loading direction to promote twinning, denoted here as T composites. To further elucidate the effects of crystalline inclusions, a number of monolithic metallic glass samples are also prepared using the same procedure; these are denoted as M samples.

4. Observed responses to deformation

Each composite sample is tested via simulated uniaxial compression. The system is subject to a constant compressive strain rate of 10 \( \mu \)s\(^{-1} \) in the \( Y \)-direction. A Parrinello–Rahman barostat which couples to the \( Z \)-direction ensures zero normal stress on the \( X-Y \) plane. The system has periodic boundary conditions in both the \( Y \)- and \( Z \)-directions and free surfaces on the \( Y-Z \) plane. The presence of the free surfaces is crucial to permit shear band formation [25]. The stress–strain curves of three types of composite samples as well as of the monolithic amorphous samples are shown in Fig. 2. For R, N, and T composite samples, each curve is averaged over 18 compression tests. For M samples, the stress–strain curve is averaged over six compression tests.

Several differences in mechanical response can be noted by direct comparison of the stress–strain curves presented in Fig. 2. It is apparent that, depending on the orientation of the crystallites, the samples exhibit different elastic moduli and ductility. Samples that favor twinning have the highest elastic modulus and the maximum stress occurs at 3.3% strain, the lowest of the composites. Samples that suppress twinning have the lowest elastic modulus and the maximum stress is higher and occurs at a larger strain than the other composites. The curve for samples with random orientation lies in between these extremes. There is no apparent enhancement in ductility in the composite samples as compared to the pure glassy samples. In fact the strength and ductility in the nanocomposite samples appears to be lower than the monolithic glass for reasons that we will discuss below.

We employed two means of analysis to study the correlation between deformation and structural changes in the material. The plastic deformation is identified by locating those regions with high local deviatoric shear strain as calculated from the atomic displacements [31]. By further analyzing the local strain information, we use the deformation participation ratio (DPR) to quantify the degree of strain localization [25,28]. DPR is defined as the percentage of atoms that have a local shear strain higher than the nominally imposed strain after mechanical deformation. Therefore, DPR ranges from zero, which corresponds to ideal localized deformation, to ½, corresponding to ideally homogeneous deformation. Furthermore, the local

![Fig. 1. Potential energy distribution for a bcc crystallite (a) precipitated from melt and (b) inserted ex situ. The potential energy ranges from \(-0.22\) (yellow) to \(-0.572\) eV (red). Graph (c) shows the average potential energy across the crystallite–amorphous interface. The left is the crystalline phase and the right is the amorphous phase.](image1)

![Fig. 2. Stress vs. strain curves for composites R (red), N (green), T (blue) as well as glassy sample M (black). All the curves from composites are calculated by averaging 18 independent samples and the curve for M is from averaging six independent samples. Error bars show the sample-to-sample variation. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)](image2)
structure around each atom is characterized by the connectivity of its first and second neighbor shell atoms. In this way, we determine whether each atom resides in a bcc structure or one of four types of Frank–Casper structure (CN12–CN16) [32] as described in Ref. [25]. These Frank–Casper structures characterize the glassy matrix.

In order to illustrate the deformation behavior of the glassy phase as a function of crystalline inclusions, Fig. 3 shows representative strain maps for N and T composites and the monolithic glass after undergoing uniaxial compression. For all the composite samples, the initial deformation occurs at the interfaces and further deformation occurs primarily in the amorphous region as well as some twinning in R and T samples. The twinning is distinguishable by its spatial extent and the specific value of the twinning strain. For N samples, which do not favor twinning, multiple shear bands are formed. In those cases, crystallites are observed to block shear band propagation resulting in shear band bending and branching. On average, the DPR in the glassy matrix is slightly higher for M, N, and R samples (36 ± 3%) than for T samples (33 ± 2%). On the other hand, the DPR for BCC phase is 5 ± 1% for N samples, 11 ± 1% for R samples and 14 ± 2% for T samples. Therefore, the bcc crystallites in N composites act primarily as obstacles for shear bands, which is in clear contrast to the crystallites in the R and T samples that more readily participate in the shear band propagation via twinning.

During the course of compression, we also observe that the growth of bcc crystals depends on the orientation of the crystallites as listed in Table 1. For N samples, there is an average 5.3 ± 0.3% increase of number of atoms in the bcc environment from 0 to 10% strain. Here we use the N composite compression test shown in Fig. 3 as an example. Before the compressive load is applied, 37.5% of atoms are in bcc local structural states as shown in Fig. 4a. At 10% strain, 39.3% of atoms are in bcc local structural states as shown in Fig. 4b. By comparing the local state of each atom at 0% strain and 10% strain, we observe an interchange of atoms between the amorphous matrix and the bcc nanocrystals. This involves simultaneous processes of dissolution and growth of the bcc nanocrystals. Fig. 4c shows that those atoms that have joined bcc crystallites (blue) and those that have left (red). Both structural transitions happen in the vicinity of interfaces during deformation. By comparison, R samples only exhibit 2.8 ± 0.3% bcc crystal growth and T samples exhibit even less growth, 0.7 ± 0.4%. This is because in those samples, bcc crystallites participate in the plastic deformation via twinning which diminishes the effect of mechanically assisted crystal growth.

In order to study the strain rate dependence of crystal growth, simulations were also performed at a rate of compression 10 times higher. For all samples, low strain rate enhances crystal growth as shown in Table 1. For instance, dissolution of bcc nanocrystals dominates in T samples at high strain rate. However, for the same samples at low strain rate, dissolution and growth processes compensate each other so that there is nearly no net change of the number of atoms in the bcc crystalline state.

Table 1

<table>
<thead>
<tr>
<th>Samples strain rate (μs⁻¹)</th>
<th>R samples (%)</th>
<th>N samples (%)</th>
<th>T samples (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.2 ± 0.3</td>
<td>2.4 ± 0.3</td>
<td>−2.2 ± 0.4</td>
</tr>
<tr>
<td>10</td>
<td>2.8 ± 0.3</td>
<td>5.3 ± 0.3</td>
<td>0.7 ± 0.4</td>
</tr>
</tbody>
</table>

Fig. 3. Representative deformation morphologies are shown for the N and T composites and the monolithic glass (M). Atoms are colored according to the local deviatoric shear strain at 10% in a compression test. Red represents 0% strain and yellow represents 10% strain. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)
The first simulated behavior that we wish to address is the apparent decrease in strength and ductility with the addition of nanocrystallites. We note that the initial plastic deformation always happens at the interfaces between the nanocrystallites and the glassy matrix for two reasons. The atoms at the interfaces have a higher potential energy than both the glassy matrix and the crystalline phase, as shown in Fig. 1c, and stress concentrations are induced by the difference of elastic moduli between the glassy matrix and the crystalline phase. Thus one reason for the lower strength and ductility appears to be the weakening from the introduction of crystal–amorphous interfaces.

Another factor in this lack of ductility is the nanofiber geometry induced by the imposition of a thin third dimension. The ability of the crystallites to block shear bands depends on the geometry and the size of the system. One simple geometric consideration for effective blocking of shear band is to see whether arbitrary planes along the direction of maximum shear will intersect inclusions. The same volume fraction of crystalline inclusions introduced in a truly three dimensional system would be more effective in blocking shear band propagation than the wires in the thin slab geometry considered here. Moreover, the spatial extent through which the shear band must propagate is also crucial in determining the inclusion–shear band interaction. Thus, for the system simulated here, which is thin in the X-direction, a high fraction of crystalline phase is required to generate multiple shear band formation [9]. In certain cases, there is not enough amorphous phase for shear bands to detour around the crystalline inclusion, or for the formation of new shear bands. Instead, the sample fails via cleavage of the crystalline–amorphous interfaces. This further enhances the issue of softening due to the crystal–amorphous interfaces. Nevertheless the features that appear in the simulated mechanical tests on those composite systems, including incipient plasticity at the interfaces, phase transformations induced by shear and shear band branching, are similar to those observed in experiments [5,7,9,21].

Although the system size effects and weakening due to interfaces dominate, we do observe some effects that we believe cause enhancement of ductility. One of these is the deformation-induced change in microstructure. It is apparent from these simulations that deformation cannot only amorphize crystallites but can also facilitate dynamic crystallite growth. During deformation, however, the compressive pressure enhances the driving force for crystallization and elevated temperature increases the kinetic rates of these processes. To confirm the crucial role played by mechanical deformation in the crystal growth, we perform three simulations for comparison. In one an uncompressed sample is annealed at 75 K. In another, an uncompressed sample is annealed at 187 K, the final temperature, at 10% strain. In the last, we simulated a sample compressed to 0.73 GPa, the hydrostatic compressive pressure at the maximum stress, and then annealed at 187 K for the same amount of time as in the compression test. In these simulations we observe −0.1%, 1.1%, and 0.7% increases in the number of atoms with bcc local environments as compared to an average 5.3% increases in the compression test for N samples. These results provide us with the confidence that plastic deformation is crucially important for the occurrence of crystal growth in these simulations, and that the elevated pressure and elevated temperature that accom-
pany the plastic deformation play only secondary roles in facilitating crystal growth at these low temperatures. It should be noted that, as shown in Table 1, low strain rate enhances crystallization, which suggests that such deformation-induced processes are likely thermally activated. We contend, however, that such thermal activation would be insufficient in the absence of the accompanying plasticity.

Such dynamically induced precipitation also hinders further plastic deformation because bcc crystallites are harder to deform than the amorphous matrix. For the compression test shown in Fig. 4, from 5% to 6% strain, 1210 atoms transform from amorphous to bcc and 64,074 atoms remain in the amorphous state. However only 3.5% of those newly transformed bcc atoms undergo a larger than 5% strain during subsequent deformation from 6% to 7% imposed strain. This is in contrast to the 16.8% of the atoms that remained amorphous which exhibited deformation during the same strain increment. Once the plastic flow triggers the growth of bcc crystallites, the shear band either must detour or a new shear band must nucleate.

6. Conclusions

We have simulated the synthesis and mechanical testing of model nanocrystallite–metallic glass composites under uniaxial compression. Features of the deformation morphologies of the composites are similar to those observed in experiments, including: (1) deformation initiated at the interfaces; (2) the bending of shear bands around crystallites resulting in propagation in an orientation away from maximum shear direction; and (3) blocking of shear bands by crystallites. Several factors affect the overall mechanical behavior upon the introduction of the crystalline phase into the amorphous matrix. The dominant effect in these simulations is the presence of weak amorphous–crystalline interfaces which play a dual role in that they weaken the entire specimen and also provide multiple locations for shear band initiation. A second factor is the resistance to plastic deformation of the crystalline inclusion when a shear band tries to propagate through. For the model composite system studied here, crystallites that can be twinned have a lower resistance which is less effective in blocking shear band propagation. The third factor is shear-induced crystal growth. The newly formed crystalline phase is much less likely to participate in further deformation, thus impinging on shear band activities. Such growth is neither the result of heating due to mechanical work nor due to the presence of compressive strain.

Acknowledgments

This work was supported by the National Science Foundation under Award No. 0135009 and in part under Grant No. PHY99-07949. The authors would like to thank Dr. Michael Atzmon and Dr. David Rigney for stimulating discussions. We also thank the Center for Advanced Computing (CAC) at the University of Michigan for providing computational support.

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