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Simulation study of mechanical properties of bulk metallic glass systems: martensitic inclusions and twinned precipitates

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Abstract

Monolithic bulk metallic glasses (BMGs) exhibit a unique combination of mechanical properties, such as high strength and large elasticity limits, but the lack of ductility is considered the main Achilles’ heel of BMG systems. To increase the competitiveness of BMGs vis-à-vis conventional structural materials, the problem of catastrophic failure via intense plastic strain localization (‘shear banding’) has to be addressed. Recent experimental observations suggest that the addition of structural heterogeneities, in the form of crystalline particles, to BMG systems hinders the catastrophic propagation of shear bands and leads to enhanced ductility. These structural heterogeneities can be introduced by either forming BMG composites, where second-phase crystalline particles accommodate applied loads via martensitic transformation mechanisms, or developing glassy alloys that precipitate crystalline particles under deformation, a process by which further deformation can be sustained by twinning mechanisms in the crystalline phase. In this work, we present a non-linear continuum model capable of capturing the structural heterogeneity in the glassy phase and accounting for intrinsic work hardening via martensitic transformations in second-phase reinforcements in BMG composites and deformation twinning in precipitated crystalline particles. Simulation results reveal that in addition to intrinsic work hardening in the crystalline phase, particle size greatly affects the overall mechanical behavior of these BMG systems. The precipitation of crystalline particles in monolithic BMGs yields
two-phase microstructures that promote more homogeneous deformation, delay
the propagation of incipient shear bands, and ultimately result in improved
ductility characteristics.

Keywords: phase-field modeling, mechanical properties, bulk metallic glass

(Some figures may appear in colour only in the online journal)

1. Introduction

Bulk metallic glasses (BMGs) have emerged as a class of structural and functional materials
systems with unique combinations of mechanical and chemical properties, such as high
strength, large elasticity limit, and corrosion and wear resistance [1–4]. Deformation
mechanisms of BMGs in response to various loading scenarios have been the subject of
intense research exploration [5, 6]. At room temperature, experiments reveal that monolithic
BMGs typically fail in a catastrophic manner with very limited global plasticity, an Achilles’
heel that hinders the use of BMGs in structural applications [7–9]. Owing to their lack of
‘microstructure’, plastic flow in BMGs ensues via the formation and propagation of highly
localized regions of intense strain, commonly referred to as shear bands [10–12].

Enhancement in ductility of BMGs can be attained by introducing structural
heterogeneities, albeit at different length scales, which can act as either seed points that promote
a more spatially distributed state of deformation, or arrest barriers to shear band propagation.

The introduction of such heterogeneities can be done by forming BMG composites, where
second-phase reinforcements are incorporated into the glassy matrix phase [13–16]. Recently,
a new class of BMG alloys has been developed, where under mechanical deformation, these
alloys precipitate nano-sized crystalline particles that promote the formation of multiple shear
bands and hinder the propagation of a catastrophic single band, thus improving the overall
ductility [17, 18].

Generally, BMG composites are formed ex situ by adding reinforcement particles into
the glassy matrix [19], or in situ by partial crystallization of the BMG alloy [6]. Ductile
second-phase particles act as both nucleating sites for shear bands and arrest barriers to shear
band extension, thus allowing a more homogeneous and distributed state of deformation
[20, 21]. The elastic mismatch between the ductile particles and glassy matrix guides the
propagating shear bands towards these domains, where further deformation is accommodated
via dislocation-mediated plasticity in the crystalline particles [13, 14, 22]. The mechanical
properties of BMG composites are optimized with respect to the volume fraction, morphology
and length scale of the second-phase reinforcements [19].

Recently, BMG composites have been developed, where second-phase reinforcements
exhibit extensive work hardening via twinning or martensitic phase transformation
mechanisms [23–26]. Transformation-induced plasticity in the crystalline particles along with
the complex interaction between the nucleated shear bands and crystalline domains lead to
BMG composites with appreciable working hardening and enhanced ductility [27, 28]. Very
recently, monolithic BMG alloys were developed such that under deformation, they precipitate
crystalline particles, which are capable of work hardening via twinning. Crystalline particles
attract shear bands that nucleate in the glassy phase and accommodate further deformation via
twinning, thus arresting the propagation of shear bands [29, 30].

Most studies on transformation-induced plasticity in BMG composites do not examine
the role of microstructure of the crystalline particles on the overall deformation behavior of
BMG composites. Furthermore, in monolithic BMGs that precipitate crystalline particles
under deformation, the interplay between propagating shear bands and geometric features of the precipitated phase has not been fully elucidated. On the other hand, existing theoretical and computational treatments of plasticity in BMGs are atomistic ones that are hard to scale up [31–37] or mesoscale ones that utilize the shear transformation zone (STZ) model to only treat monolithic BMGs [38–42]. Other mesoscale models for BMG composites do not account for work hardening in the crystalline phase via martensitic transformation nor do they capture deformation-induced precipitation of crystalline phase that undergo twinning upon further deformation [43–45].

In this work and starting with a recently introduced model for BMG systems [46, 47], we develop a diffuse-interface approach for the precipitation of crystalline particles in monolithic BMGs under deformation and their subsequent work hardening via deformation twinning. Simulation results provide quantitative insights into the role of area fraction of the precipitated phase and its characteristic spatial length scales on the mechanical properties of these BMG systems. Additionally, we utilize the model to examine the behavior of BMG composites, whose second-phase reinforcements work-harden via martensitic transformations. Our results highlight the importance of area fraction and geometric attributes of crystalline particles on the overall ductility and strength of these systems. In particular, for a given area fraction of the ductile phase, smaller particles yield BMG microstructures that exhibit better ductility characteristics than the ones with larger particles. Furthermore, for a given area fraction, mono-

2. Theoretical background

The starting point of our diffuse-interface model is the introduction of a total free energy of a mechanically deformed BMG system. The general framework is developed such that it is capable of (a) capturing the mechanical behavior of BMG composites, whose second-phase reinforcements work-harden via martensitic transformations; we refer to these systems as ex situ composites and (b) accounting for the precipitation of crystalline domains in the case of monolithic BMGs under an applied stress. Once these crystalline domains nucleate, they work-

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angle $\theta$, we write the strain tensor in the primed reference as $\epsilon_\alpha' = \Lambda_{1\alpha}(\theta)\epsilon_\alpha$, where $\Lambda_{1\alpha}(\theta)$ is an orthogonal rotation matrix [49]. Within this rotated configuration, the strain measures become $\epsilon_1' = \epsilon_1$, $\epsilon_2' = \epsilon_2 \cos(2\theta) + \epsilon_3 \sin(2\theta)$, and $\epsilon_3' = \epsilon_2 \cos(2\theta) - \epsilon_3 \sin(2\theta)$, where the dilatation strain $\epsilon_1$ is invariant under rotation, as expected [50].

According to the above re-arrangements of the strain components, an additive decomposition for the total free energy $F_{\text{tot}}$ of a BMG system is adopted such that

$$F_{\text{tot}}[u, \psi] = \int \text{d}r f_{\text{tot}} = \int \text{d}r \left\{ z(\psi)f_{\text{glass}} + \left[1 - z(\psi)\right]f_{\text{trans}} + f_{\text{prec}} \right\},$$

(1)

where $z(\psi)$ is a smooth interpolation function, such that $z \rightarrow 1$ (0) in the glassy (crystalline) phase. Furthermore, $f_{\text{glass}}$ is the deformation free energy density of the glassy phase, while $f_{\text{trans}}$ is an energy density term that accounts for the work hardening in the crystalline phase via martensitic transformations in ex situ BMG composites or deformation twinning in the case of monolithic BMGs. In addition, $f_{\text{prec}}$ denotes the chemical free energy density associated with the precipitated crystalline phase in monolithic BMGs. According to our recently developed model for BMG systems [46] and motivated by the treatment of plasticity in 2D systems [48], the deformation energy of the glassy phase $f_{\text{glass}}$ is written as

$$f_{\text{glass}} = \frac{K_g(r)}{2} \epsilon_1^2 + \frac{K_g(r)}{2} \epsilon_2^2 + \frac{\mu_g(r)}{2} \Delta \epsilon^2 + \frac{W^2}{2} \left[ (\nabla u_x)^2 + (\nabla u_y)^2 + 4 (\nabla \epsilon_r)^2 \right].$$

(2)

Under the isotropy assumption, $K_g(r)$ and $\mu_g(r)$ denote the bulk and shear moduli for the glassy matrix, respectively, while the field $\Delta(r)$ sets the local shear strain that each local glassy element has to experience in order to undergo a local slip event. Furthermore, the energy barrier for such a transition is $\mu_g \Delta^2/(4 \pi^2)$. To account for the structural heterogeneity in the glassy phase, $\Delta(r)$ is assumed to be a quenched, Gaussian random field with average $\langle \Delta(r) \rangle = \Delta_0$ and a two-point correlation function $\langle [\Delta(r) - \Delta_0][\Delta(r') - \Delta_0] \rangle = \sigma^2 \exp(-|r - r'|/\xi)$, where $\sigma^2$ and $\xi$ denote the variance of the distribution and a structural correlation length, respectively [46]. The last term in equation (2) contains higher order gradients in the displacement field, and is introduced to regularize strain gradients on scales $\lessapprox W_0/\sqrt{\pi W_0}$. Finally, in the small strain limit and in the absence of interfaces, $f_{\text{glass}} \approx K_g \epsilon_1^2/2 + \mu_g \epsilon_2^2/2 + \mu_g \epsilon_3^2/2$ reduces to the linear isotropic elasticity for 2D systems [50].

Next, $f_{\text{trans}}$ is introduced to account for the local deformation energy within the crystalline domains. The general description for $f_{\text{trans}}$ is comprised of the standard quadratic elastic energy terms and additional non-linear energy terms that for the case of ex situ BMG composites, allow for work hardening in the crystalline domains via martensitic transformation, while in monolithic BMGs that precipitate crystalline particles, it accounts for deformation twinning within these particles. Motivated by the treatment of deformation twinning by Heo et al [51] and under the assumption of cubic symmetry of the crystalline phase, $f_{\text{trans}}$ is written in terms of the strain measures in the primed frame as

$$f_{\text{trans}} = \frac{K_c}{2} \epsilon_1^2 + \frac{\mu_c}{2} \epsilon_3^2 + \frac{C}{2} \epsilon_2^2 + f_{\text{high}} + \frac{W^2}{2} |\nabla \epsilon_r'|^2,$$

(3)

where $K_c$ and $\mu_c$ denote the bulk and shear moduli of the crystalline phase, respectively. In terms of the elastic moduli for a crystal with cubic symmetry, $C_{11}, C_{12}$, and $C_{44}$, $K_c = C_{11}/d + (d - 1)C_{12}/d$, $\mu_c = C_{44}$ and $C = (C_{11} - C_{12})/2$, where $d$ is the dimensionality of the system ($d = 2$ in the present work). The non-linear, non-quadratic part of the elastic energy, $f_{\text{high}}$, contains higher order polynomials of the tetragonal strain $\epsilon_2'$ and is expressed as

$$f_{\text{high}} = \frac{\alpha_0}{4} \epsilon_2'^4 + \frac{\alpha_1}{6} \epsilon_2'^6 + \beta \epsilon_2'^2 \epsilon_1'.$$

(4)
where $\alpha_o, \alpha_1$ and $\beta$ are the higher order non-linear elastic constants, while $W_t$ in equation (3) is the strain gradient coefficient that sets the energy cost of creating a domain wall between transformed or twinned regions. The constant $\beta$ couples the hydrostatic and tetragonal strain measures and phenomenologically accounts for areatric changes during structural transformations. In this work, $e'_2$ is regarded as an order parameter that for the case of martensitic transformation describes a 2D transition from square to two rectangular variants, while for the case of deformation twinning, $e'_2$ describes the transformation from the parent crystal to two twinned variants, as will be discussed below.

With the proper choice of the parameters $\hat{C}, \alpha_o, \alpha_1$ and $\beta$, $f_{\text{trans}}$ can be utilized to capture both martensitic transformation in the crystalline phase in \textit{ex situ} BMG composites and deformation twinning in the crystalline domains that precipitate in monolithic BMGs. In the case of martensitic transformations, the driving force for this structural transformation is the difference between the free energy densities between the parent and martensitic phases [52]. In this work, we consider a 2D square-to-rectangular transition, where the metastable square parent crystalline inclusion described by $e'_2 = 0$ is transformed into two states described by $e'_2 = \pm \xi_m$ corresponding to the two rectangular variants [53–55]. This is illustrated schematically in figure 1(a), where the minima of $f_{\text{trans}}$ correspond to the rectangular variants. The applied strain serves as an external field that favors one of the rectangular variants, the behavior of which is schematically depicted in figure 1(c). For monolithic BMGs, which precipitate crystalline particles that subsequently work-harden via deformation twinning, the free energy density of the parent crystal and that of the twinned state is the same, i.e., there is no thermodynamic driving force for the transition from the parent to twinned states [51]. An energy landscape for this case is depicted in figure 1(b), where within the crystalline phase, the minima corresponding to the parent phase and twinned variants are identical. As depicted in figure 1(d), the mechanical energy associated with the externally applied strain favors either of the twinned variants over the parent one [51, 56, 57].

Within the crystalline phase, $\theta = \theta(r)$ is a field that defines the orientation angle between the local ‘primed’ frame in the crystalline phase and the global one, while $\theta$ is set to zero in the glassy phase. In both martensitic transformation and deformation twinning cases, if the transformation strain $e'_2 = \pm \xi_m$, i.e. the minima of the free energy $f_{\text{trans}}$, then the angle $\theta$ determines the contribution of the shear $e_3$ and tetragonal $e_2$ strains to $e'_2$, where this dependency is described by $e'_2 = e_3 \cos(2\theta) + e_2 \sin(2\theta)$. In particular, the absolute minima of $f_{\text{trans}}$ correspond to the tetragonal strain, $e_2$, when $\theta = 0$, while for $\theta = \pi/4$, the minima correspond to pure shear deformations.

Next, $f_{\text{prec}}$ is the chemical free energy term associated with the crystalline phase that precipitates in monolithic BMGs due to mechanical deformation. As in standard phase-field treatments, $f_{\text{prec}}$ is written as

$$f_{\text{prec}} = A \left[ g(\psi) + \frac{W_\psi}{2} |\nabla \psi|^2 \right],$$

(5)

where $A$ is a constant that sets the energy scale and $g(\psi) = \psi^4/4 - \psi^2/2$ is a fourth-order Landau polynomial, whose minima $\psi = -1$ and $+1$ correspond to the glassy and precipitated crystalline phases, respectively. The parameter $W_\psi$ is a gradient energy coefficient that sets the energy of the glassy–crystalline interface. Here, the role of $f_{\text{prec}}$ merits some attention. In the case of \textit{ex situ} BMG composites with crystalline domains undergoing martensitic transformation, the spatial distribution of the crystalline phase within the glassy matrix is already determined; thus, the $\psi$ field is a static, non-evolving one. Details on how these BMG composites are prepared in our model will be discussed in the next section. On the other hand, for monolithic BMGs, the nucleation and growth of crystalline domains due to
Figure 1. Schematic of \( f_{\text{trans}} \) for an undeformed (a), (b) and mechanically deformed (c), (d) BMG system. (a) A BMG composite, where the shaded domain represents a crystalline particle that undergoes a martensitic transformation from square to two rectangular variants. (b) Precipitation of a crystalline domain, shaded region, in a monolithic BMG, where a transformation from the parent crystal to two twinned variants occurs due to deformation twinning. In both cases, the applied strain acts as the external field that favors one of the variants over the pristine state with \( e'_2 = 0.0 \).

As far as the kinetic equations are concerned, we treat \( \psi \) as a conserved order parameter in order to control the overall area fraction of the precipitates, while the displacement field \( u(r, t) \) is a non-conserved one. Hence, the variational evolution equations follow from

\[
\frac{\partial^2 u_i}{\partial t^2} - \eta \nabla^2 \frac{\partial u_i}{\partial t} = -\Gamma \frac{\delta F_{\text{tot}}}{\delta u_i}, \quad i = x, y, \tag{6}
\]

\[
\frac{\partial \psi}{\partial t} = \nabla \cdot \left( M \nabla \frac{\delta F_{\text{tot}}}{\delta \psi} \right) + \zeta(r, t). \tag{7}
\]

Here \( \eta \) and \( \Gamma \) are the effective viscosity and elastic wave speed \([46, 54]\). The statement of mechanical equilibrium can be deduced from equation (6) by noting that \( \delta F_{\text{tot}} / \delta u_i = -(\partial / \partial x_j)(\delta f_{\text{tot}} / \delta u_i) = -(\partial / \partial x_j)(\delta f_{\text{tot}} / \delta \epsilon_{ij}) = -\partial \sigma_{ij} / \partial x_j \). Therefore, at a given prescribed...
applied strain, the heavily damped wave equation, equation (6), is used to equilibrate the displacement field with the right-hand side acting as the driving force. Next, the evolution of the \( \psi \) field follows from the conserved Cahn–Hilliard kinetic equation, equation (7), where \( M \) is a mobility parameter and \( \xi \) denotes the thermal noise with the correlation function \( \langle \xi(r, t)\xi(r', t') \rangle = -2\bar{T}M^2\delta(r-r')\delta(t-t') \) in accordance with the fluctuation dissipation theorem, where \( \bar{T} \) denotes the strength of the noise [54]. This phenomenological form of the evolution equation is motivated by the experimental observation that only a finite volume fraction of the glassy phase crystallizes during the deformation process [29, 30]. The driving force for the evolution of \( \psi \) is expressed as \( \delta\mathcal{F}_{\text{tot}}/\delta\psi = (\partial z/\partial\psi)(f_{\text{glass}} - f_{\text{trans}}) + A(\partial g/\partial\psi) - W_{\psi}\nabla^2\psi \). It is worth noting that in the case of BMG composites, where the crystalline phase undergoes martensitic transformation, the static nature of the \( \psi \) field can be enforced by setting \( M = 0 \). On the other hand, for monolithic BMGs, which under deformation precipitate crystalline domains, the spatio-temporal evolution of these domains is captured through the kinetic equation for \( \psi \), equation (7), with a non-zero \( M \). Furthermore, the spatial average of \( \bar{\psi} \), \( \bar{\psi} \), both controls the onset of crystalline phase precipitation in monolithic BMGs due to the externally applied strain and determines the final area fraction of the crystalline phase particles which undergo deformation twinning. In the simulations, it is enforced by setting \( \psi(r, 0) = \bar{\psi} \) initially in the precipitate system.

3. Results and discussion

Having outlined our theoretical approach above, we now focus on the deformation behavior of two BMG systems, namely (i) BMG composites where the crystalline domains accommodate deformation via martensitic deformation, and (ii) monolithic BMGs, which, under deformation, precipitate a crystalline phase that subsequently deform by twinning.

3.1. BMG composites with martensitic inclusions

We first examine the role of crystalline phase microstructure, i.e. particle size and area fraction, and the associated martensitic transformation mechanisms on the mechanical behavior of \textit{ex situ} BMG composites. Crystalline domains are idealized as circular particles and ‘virtual’ BMG and the associated martensitic transformation mechanisms on the mechanical behavior of ex situ BMG composites. Crystalline domains are prepared by randomly placing these domains in a glassy matrix. For a given area fraction \( \phi_{\text{a}} \) of the crystalline phase, the design parameters are the total number and particle radius of the crystalline domains. BMG composites systems are then digitized to yield 256 × 256 square lattices. BMG composites are simulated under simple shear, where the top edge is displaced horizontally relative to the fixed bottom one, while periodic boundary conditions for the displacement field are used lengthwise. Stresses are measured in units of crystalline phase shear modulus, while length scales are expressed in terms of the structural correlation length \( \sim 5 \text{nm} \). The dynamical equations for the displacement field are solved with \( \Delta x = \Delta y = 1.0 \) and a dimensionless time step \( \Delta t = 0.003 \). The parameters \( \eta \) and \( \Gamma \) are set to 80 and 240, respectively, to ensure that stresses relax effectively instantaneously relative to the externally imposed (non-dimensional) strain rate \( 2 \times 10^{-4} \). Elastic constants for the glassy and crystalline phases are set to \( (K_g, \mu_g, K_c, \mu_c) = (9, 3, 3, 1) \). In the glassy phase, the random field \( \Delta \) is generated such that \( (\Delta(r)) = 0.6 \) with \( \sigma^2 = 0.0125 \) and \( \xi = 2 \). For the crystalline phase, the elastic constants in \( f_{\text{trans}} \) are chosen such that the metastable state corresponds to the parent (undeformed) phase and the global minima represent the martensite (deformed) phase. A suitable choice for these parameters is \( (C, \alpha_0, \alpha_1, \beta) = (0.01, -40.0, 750.0, 0.0) \), corresponding to \( \xi_{\text{m}} = 0.23 \). Here, we note that the parameter \( \beta \) accounts for area changes due to solid structural transitions. In 2D systems, area changes due to martensitic transformation
Figure 2. Shear strain contours for a BMG composite with an area fraction $\phi_m = 35\%$ of the crystalline phase, at a fixed orientation $\theta = 0$ (a)–(c), and $\theta = \pi/4$ (d)–(f), at a nominal strain of 5.4% (a), (d); 8.7% (b), (e); and 13.0% (c), (f). Boundaries of crystalline phase particles are indicated in black.

are negligible, justifying the use of $\beta = 0$ [58]. Other parameters that are used in the simulation are set to $(W_\psi, W_t, W_g) = (0.0, 1.0, 1.0)$. The crystalline phase in ex situ BMG composites is already defined and does not evolve spatially or temporally; therefore, the field $\psi$ is a static one and its contribution to the total energy is not included. This is achieved by assigning the model parameter $\Lambda$ and the mobility $M$ to $\Lambda = M = 0.0$. The threshold value $\psi_0$ that sets the transition between glassy and crystalline phases is set to 0.10. Finally, to explore the role of the preferential direction for martensitic transformation in the crystalline phase, i.e. the orientation angle $\theta$, on the mechanical behavior of BMG composites, we simulate two extreme cases, where in the first one, $\theta = 0$ in the crystalline phase, which indicates that the martensitic transformation strain, $e'_2$, is accommodated as tetragonal strains, $e_2$. In the second case, $\theta = \pi/4$ indicating that the transformation strain is completely accommodated as shear strain, $e_3$. To account for sample-to-sample variations, results for each simulation are averaged over five independent runs.

We begin our exploration of the model by qualitatively examining the role of orientation angle $\theta$ in the crystalline phase on the mechanical of ex situ BMG composites. For a BMG composite with an area fraction $\phi_m = 35\%$ of the crystalline phase and $\theta = 0$, panels (a), (b) and (c) of figure 2 are contours of shear strain at nominal strains of 5.4%, 8.7% and 13.0%, respectively. It can be seen that initially (see panel (a)), applied strain is accommodated in the crystalline particles. As the applied strain level increases, multiple shear bands start to nucleate in the glassy matrix and interact with the crystalline particles (panel (b)). At late stages, a single shear band has propagated across the entire sample (panel (c)). On the other hand, for a BMG composite with the same area fraction of the crystalline phase, $\phi_m = 35\%$, but with $\theta = \pi/4$, panels (d), (e) and (f) of figure 2 depict contours of shear strain at the same nominal
strain levels. It is evident that the BMG composite with $\theta = \pi/4$ is capable of accommodating applied strain in the crystalline particle up to large nominal strain levels. By comparing shear strain contours for the BMG composite with $\theta = 0$ (see figures 2(a)–(c)) and the one with $\theta = \pi/4$ (see figures 2(d)–(f)), it can been seen that the composite with $\theta = \pi/4$ is capable of accommodating larger strain levels in the crystalline phase, which subsequently delays the onset of shear band nucleation (see figures 2(b) and (e)). Furthermore, at a nominal strain of 13% the degree of strain localization within the shear band in the BMG composite with $\theta = \pi/4$ is considerably less than the one with $\theta = 0$, which can be an indication that ductility can be enhanced via tailoring the preferential direction of the crystalline phase for martensitic transformation. This can be explained by realizing that for the composite with $\theta = \pi/4$, the transformation strain, $e_2^\prime$, is accommodated as shear, $e_3$, in the crystalline phase, which is the operating mode of deformation, i.e. the samples are under simple shear deformation.

To quantify the effects observed in figure 2, we turn our attention to the stress–strain curves for these systems. The stress–strain curves for \textit{ex situ} BMG composites with $\phi_m = 35\%$ of the crystalline phase and particle radius $\sim 7$ with $\theta = 0$ and $\pi/4$ along with a representative monolithic BMG are shown in figure 3(a). It can be clearly seen that for the BMG composite with $\theta = 0$ the introduction of second-phase crystalline particles does not lead to significant changes in ductility and mechanical strength in comparison with the monolithic BMG. On the other hand, considerable plastic flow albeit accompanied with lower mechanical strength is observed in the composite with $\theta = \pi/4$.

To examine the role of crystalline phase microstructure, several BMG composites are examined with various particle sizes and area fractions $\phi_m$ of the crystalline phase. For each BMG composite, the strain at the peak point in the shear stress–strain curve is identified as the ultimate strain, $\gamma_f$, and recorded as a function of area fraction, $\phi_m$, and crystalline particle radius, $R$. Figures 3(b) and (c) are plots of $\gamma_f$ as a function of particle radius at several area fractions for BMG composites with $\theta = 0$ and $\pi/4$, respectively. Under both assumptions
for the orientation angle $\theta$, it can be seen that the introduction of smaller crystalline particles leads to higher ultimate strain, $\gamma_1$. Furthermore, for the BMG composite with $\theta = \pi/4$ (see figure 3(c)) a trend exists, where an increase in the area fraction $\phi_n$ of the crystalline phase leads to enhancement in the ductility characteristics of these composites. This trend of ductility versus area fraction of the crystalline domains is less pronounced for BMG composites with $\theta = 0$ (see figure 3(b)). This behavior can be explained as follows. In our simulations, BMG samples are loaded in a simple shear configuration, where the top edge is displaced with respect to the bottom one. Now, for the case of $\theta = \pi/4$, area elements within the crystalline particle are aligned with the loading configuration, which in turn allow them to accommodate the applied strain. For the BMG composites with $\theta = 0$, on the other hand, the transformation strain is accommodated as tetragonal strain, $e_2$, which is not a configuration that is favorably aligned with the loading direction. The results depicted in figures 3(b) and (c) suggest that the ductility of BMG composites, where the ductile phase accommodates applied strain via martensitic transformation, can be enhanced by increasing the area fraction of the ductile phase $\phi_n$ and reducing the effective size of the ductile particles.

3.2. Strain-induced precipitation and deformation twinning in monolithic BMGs

Next, monolithic BMGs, which under externally applied strain precipitate crystalline phase particles that subsequently deform by twinning, are examined. As discussed in section 2, the spatio-temporal evolution of the crystalline phase particles that precipitate in monolithic BMGs is tracked via the field $\psi$. Therefore, unlike the case for BMG composites, all energy contributions in equation (1) are included, i.e. $A \neq 0$. Additionally, there is no thermodynamic driving force for the transformation of the parent crystalline phase to its twinned variants (see figure 1(b)). Instead, the externally applied strain acts as a field that favors one of the twinned variants over the pristine crystalline phase (see figure 1(d)). Similar to the treatment of BMG composites, monolithic BMGs are generated on a $256 \times 256$ square lattice. The dynamical equations for the displacement field are solved with $\Delta x = \Delta y = 1.0$ and a time step $\Delta t = 0.003$. Again, $\eta$ and $\Gamma$ were set to 80 and 240, respectively, to ensure that stresses relax instantaneously relative to the externally imposed (non-dimensional) strain rate $2 \times 10^{-4}$. Elastic constants for the glassy and crystalline phases are set to $(K_g, \mu_g, K_c, \mu_c) = (9.3, 3.3, 1.1)$.

In the glassy phase, the random field $\Delta$ is generated, such that $(\Delta(r)) = 0.6$ with $\sigma^2 = 0.0125$ and $\xi = 2$.

For the crystalline phase, the elastic constants in $f_{\text{trans}}$ are chosen such that the precipitated crystalline phase along with the twinned variants have the same energy. A suitable choice for these parameters is $(C, \alpha_0, \alpha_1, \beta) = (0.32, -32.0, 600.0, 0.0)$, corresponding to $\xi_n = 0.2$. Other parameters that are used in the simulation are set to $(W_\psi, W_t, W_\theta, A) = (1.0, 1.0, 1.0, 1.0)$. To track the spatio-temporal evolution of the precipitated crystalline phase, the kinetic equation for the $\psi$ field, equation (7), is solved with $M = 0.2$ and the strength of the noise term $\bar{T} = 0.001$. To examine the effect of the overall area fraction of the crystalline precipitate particles, we consider two monolithic BMG systems with $\psi = -0.58$ and $-0.50$ along with $\theta = \pi/4$. This specific value of $\theta$ corresponds to a transformation strain which is completely accommodated as shear strain, which is the operating mode of the externally imposed deformation in the present work.

We begin our investigation by qualitatively examining the behavior of these monolithic BMG systems under simple shear loading. Panels (a), (b) and (c) of figure 4 depict shear strain contours for the BMG with $\psi = -0.58$ at nominal shear strains of 4.0%, 8.7% and 13.0%, respectively. At low strain levels, the applied strain is entirely accommodated by the glassy phase and no precipitation of crystalline particles is observed (see figure 4(a)). Crystalline
Figure 4. Shear strain contours for a monolithic BMG with deformation-induced precipitates (which subsequently undergo deformation twinning) with $\psi = -0.58$ (a)-(c), and $\psi = -0.50$ (d)-(f), at a nominal strain of 4.0% (a), (d); 8.7% (b), (e); and 13.0% (c), (f). Boundaries of the crystalline particles are denoted in black and defined via the level set $\psi = 0$. Area fractions of the crystalline precipitates at the end of the deformation process are $\phi_p \approx 10\%$ (a)-(c) and $\phi_p \approx 35\%$ (d)-(f), respectively.

particles first precipitate at regions where the strains localize in the glassy phase. Then, these crystalline particles grow in size and partly accommodate the applied strain via twinning, as evidenced by the presence of large strains within the precipitates. At later stages of deformation, a shear band grew and propagated across the sample (see figure 4(c)). Also, it can be seen that the precipitated crystalline particles are spatially distributed throughout the glassy phase, resulting in a two-phase microstructure that can lead to enhancement in ductility due to the effective interaction between shear bands and crystalline particles. The corresponding shear strain contours for the BMG system with $\psi = -0.50$ at nominal shear strains of 4.0%, 8.7% and 13.0% are in turn shown in panels (d), (e) and (f) of figure 4, respectively. In this system, crystalline particles first appeared at a much earlier stage of the deformation process. With further deformation, more particles precipitated, resulting in an increase in the area fraction of the crystalline phase, as expected. In particular, at the end of the deformation process, $\phi_p \approx 10\%$ (panel (c)) and $\phi_p \approx 35\%$ (panel (f)), corresponding to $\psi = -0.58$ and $-0.50$, respectively. In addition to the crystalline domains becoming more numerous, they also began to display twinning behavior as the deformation proceeded, as evidenced by the accumulation of strain within the particles.

The microstructural attributes of the crystalline phase, i.e. area fraction $\phi_p$, effective particle size and spatial distribution, along with their capability of accommodating applied strain via twinning leads to a more homogeneous state of deformation (see figure 4(e)). At a nominal strain of 8.7%, it can be seen that the monolithic BMG with more crystalline particles, which deform via twinning (see figure 4(e)), results in a microstructure, where shear
band nucleation and propagation is delayed compared to the one with smaller area fraction of precipitated crystalline particles (see figure 4(b)). In both BMG systems examined in figure 4, it is evident that the crystalline phase precipitates by nucleating small seed particles, which grow with further deformation.

Next, we characterize the resulting BMG microstructures by examining the area fraction, $\phi_p$, of the precipitated phase. The evolution of $\phi_p$ as a function of the applied shear strain is shown in figure 5(a), where it can be seen that monolithic BMGs with $\bar{\psi} = -0.58$ and $-0.50$ asymptotically reach $\phi_p = 0.1$ and $0.35$, respectively. The dip in $\phi_p$ observed at large applied shear strain values is associated with the onset of shear band propagation across the sample. In addition, several monolithic BMGs are examined with various values of $\bar{\psi}$, which set the final area fraction, $\phi_p$, of the precipitated crystalline phase. The dependence of $\phi_p$ on the model parameter $\bar{\psi}$ is depicted in figure 5(b), which serves as a one-to-one map between the desired area fraction of the precipitated crystalline phase and $\bar{\psi}$.

The mechanical behavior of the monolithic BMGs studied in this section is analyzed by examining the corresponding stress–strain curves. Figure 6(a) is a plot of the shear stress–strain curves for monolithic BMGs with $\bar{\psi} = -0.58$ and $-0.50$, where the curve for a representative monolithic BMG without precipitates is plotted for comparison. It is evident that increasing the area fraction $\phi_p$ of the precipitated crystalline particles, which subsequently undergo deformation twinning, leads to BMG systems with enhanced ductility and hardening behavior. This behavior can be seen by examining the work-hardening portion of the stress–strain curve in the BMG system with $\bar{\psi} = -0.50$, i.e. $\phi_p = 35\%$, which is attributed mainly to the twinning mechanisms in the precipitated crystalline particles, which work-harden as the BMG system is deformed. It is worth noting that monolithic BMGs that precipitate a crystalline phase with relatively small area fractions do not experience a drastic improvement in ductility, refer to figure 6(a) for a BMG with $\bar{\psi} = -0.58$ ($\phi_p = 10\%$), mainly due to the lack of an effective distribution of crystalline particles, which can impede the propagation of shear bands and accommodate further deformation via twinning.
Moreover, the mechanical properties of the monolithic BMGs with various values for $\bar{\psi}$, or equivalently area fractions $\phi_p$ of the precipitated crystalline phase, are examined. Similar to the case of BMG composites, we extracted the peak points in the stress–strain curves of these systems and identified them as the ultimate strain, $\gamma_f$, and stress, $\sigma_{uts}$.

Figure 6(b) is a plot of $\gamma_f$ and $\sigma_{uts}$ as a function of the area fraction, $\phi_p$, of the precipitated crystalline phase. It can be seen that as $\phi_p$ increases, the ultimate strain, $\gamma_f$, of the BMG system monotonically increases indicating enhanced ductility, while the mechanical strength, $\sigma_{uts}$, is reduced. The trends observed in figure 6(b) provide an avenue to developing monolithic BMGs, which under mechanical deformation, precipitate a crystalline phase that can subsequently accommodate applied strain via twinning. Such BMGs are characterized by a work-hardening behavior and enhanced ductility, mechanical properties that pure monolithic BMGs lack. Based on the aforementioned results, it can be seen that the ultimate strain and strength of BMGs with twinned precipitates are functions of both their spatial distribution and twinning behavior that takes place within these particles. As depicted in figure 6(a), simulation results reveal that enhancements in ductility and hardening behavior over monolithic BMGs can be attained in systems that, when deformed, precipitate crystalline domains that subsequently absorb additional deformation via twinning.

Finally, the results for the twinned precipitates system with $\phi_p = 35\%$ are compared to the martensitic inclusions one at same area fraction of particles with a fixed orientation $\theta = \pi/4$ and identical elastic properties. From a morphological perspective, the only difference between these systems is that at late stages of the deformation process, sizes of the second phase particles are not fixed in the precipitate case. Now, upon comparing the deformation sequences in figures 2(d)–(f) and 4(d)–(f), it can be seen that both systems are characterized by homogeneously distributed strain prior to the development of a single shear band that eventually propagates through the sample. As a result of this homogeneous distribution of strain, these composites are more ductile than the pure glassy ones, as evidenced by the stress–strain data in
figures 3(a) and 6(a). Interestingly, the ultimate stress for the martensitic inclusions system is lower than the twinned precipitates one at the same crystalline phase area fraction \( \phi \), while the ultimate strain is approximately the same. This behavior can be rationalized by recognizing that while the ultimate strain is controlled by \( \phi \) and the transformation strain (which are similar in these two particular systems), the twinned precipitates system has the distinct advantage in that the soft domains precipitate during the deformation process. This delayed onset of deformation twinning leads to more effective work-hardening behavior than in the martensitic inclusions system, where such processes become operational already at the beginning of the deformation process.

4. Concluding remarks

In this study, we presented a diffuse-interface model capable of examining the mechanical behavior of (i) ex situ BMG composites, where the crystalline phase accommodates applied strain via martensitic transformation mechanisms, and (ii) monolithic BMGs, which under the action of externally applied loads, precipitate crystalline phase particles that subsequently deform via a twinning mechanism. For the case of ex situ BMG composites, the role of crystalline phase attributes, characterized by area fraction and crystalline particle size, on the mechanical properties and ductility characteristics of these systems was examined. For a given area fraction of the crystalline phase, particles were idealized as circular domains that were randomly distributed in the glassy matrix phase, resulting in two-phase microstructures. Simulation results revealed that larger area fractions of the crystalline phase and smaller particle sizes lead to higher ultimate strain values. This behavior is attributed to the resulting microstructure, where spatially distributed crystalline particles can effectively interact with incipient shear bands and accommodate applied strain via a martensitic transformation, effectively retarding the development and growth of spatially extended shear bands.

For monolithic BMGs, on the other hand, which under the action of applied strain precipitate crystalline phase particles that accommodate additional deformation via twinning mechanisms, the role of the precipitated crystalline phase and the associated deformation mechanisms on the overall mechanical behavior of these systems, were investigated. Specifically, several monolithic BMGs with various area fractions of the precipitated crystalline phase were examined. Our results demonstrate that increasing the area fraction of the precipitated phase yields BMG systems with strain-induced hardening and enhanced ductility characteristics. In comparison with BMG composite systems which include a simple ductile metallic phase investigated in our earlier work [47], allowing the metallic phase particles to either undergo a martensitic transformation or deformation twinning can impart significant improvements to the overall mechanical properties of the composite system.

In closing, we note that the model presented in this work can be utilized as a design tool to survey the phase space of microstructural attributes, e.g. volume fraction, particle size and spatial distribution of second-phase heterogeneities, and identify combinations of morphological parameters that optimize the mechanical properties of these systems. From a more general computational perspective, our approach integrates existing continuum models for the deformation behavior of both disordered [46] and martensitic [51] systems, as well as introduces a simple phenomenological kinetic model for the deformation-induced precipitation of crystalline particles (equation (7)), which subsequently undergo deformation twinning. Detailed experimental characterization work and atomistic simulations are required to further develop and inform the kinetic precipitation model, as in its current form it does not a priori predict the area fraction of the crystalline particles. We hope that the work presented herein
catalyzes new investigations (both experimental and computational) into the deformation and microstructural properties of BMG systems.

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