

Article

The Transition from Strain Softening to Strain Hardening in Metallic Glasses

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Abstract

Despite their excellent mechanical properties, metallic glasses (MGs) are significantly hindered by poor plasticity and toughness, which are essential for structural applications. The brittleness arises from the rapid propagation of shear bands (SBs), leading to strain softening and catastrophic failure. Recent advancements in microstructural engineering, particularly boundary engineering, such as nano-glass, focus on the utilization of heterogeneous structures to promote the proliferation and delocalization of SBs. Various attempts have been made experimentally to address these issues, but with very limited improvement in tensile strength and toughness. Under tensile loading, micro- or nano-pillar samples exhibit strain softening and continue to undergo plastic deformation after reaching yield or peak stress, especially the nano-glass micro-pillar. Reports on tensile strain-hardening in MG micro-pillars are rare. In this finite element simulation study, we optimize appropriate statistical and spatial distributions of free volume within the microsamples. Both the post-yield strength and the mean tangent modulus increase with progressive gradient structural modifications, thereby inducing a transition from strain-softening to strain-hardening behavior, as well as a concurrent transition from plastic fracture to brittle fracture. We systematically investigate the deformation mechanisms and transition mechanisms of fracture modes, which are closely associated with heterogeneous microstructures and their evolution in MGs. These insights into the transition mechanism could significantly facilitate the design and optimization of MGs to achieve enhanced toughness and strain hardening.

Keywords: metallic glass; transition mechanism; fracture mode; shear band; microstructure; strain hardening



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1. Introduction

Metallic glass (MG) is a structurally disordered alloy without a long-range periodic atomic order. The atomic packing makes the MG free of structural defects and microstructures, such as dislocations and grain boundaries in crystalline solids [1]. The disordered atomic structure not only gives rise to some unique properties, such as high specific strength, large elastic limit, good corrosion resistance, catalytic performance, soft magnetism, and unique net-shape formability, but also leads to some significant limitations for structural and functional applications [2]. One major drawback is the limited macroscopic plastic deformability at room temperature, especially under unconstrained tensile mode. The

brittleness originates primarily from rapid shear banding [3]. Plastic deformation of MGs is highly localized in shear bands (SBs), leading to strain softening and catastrophic failure. Therefore, the natural strategy and significant efforts to enhance their plasticity have been focused on controlling the initiation of shear banding and ensuring uniform distribution of the SBs, or preventing their propagation [4–6]. The desired phenomenological deformation mode is homogeneous plastic deformation in the MG with improved plasticity and strength. There are currently two primary approaches to achieving homogeneous plastic deformation. The first method pertains to the extrinsic size effect and involves reducing the dimensions of the MG sample [7]. For instance, when Zr-based metallic glass nanopillars are reduced to a diameter of 100 nm or below, they exhibit significant homogeneous plasticity. The limited space in nanometer-scale samples makes it more difficult for SB nuclei to develop into mature SBs. The second approach involves the incorporation of a heterogeneous structure within the MG matrix or the development of MG composites [4–6,8–10]. Recent boundary engineering, such as nano-glasses (NGs), has focused on introducing a heterogeneous structure to promote the multiplication and delocalization of SBs [11–15]. To explore the mechanisms of homogeneous deformation or identify key structural parameters in ductile MGs, one can examine micro- or nano-pillars of MGs with heterogeneous structures, such as NG nano-pillars [13,14]. The mechanical properties of a $\text{Sc}_{75}\text{Fe}_{25}$ NG were investigated through in situ tensile tests in a transmission electron microscope [15]. The NG samples with a characteristic dimension of 400 nm exhibited uniform tensile plasticity; however, the deformation after the yield point and before final failure showed strain-softening behavior [16,17]. In the experiments, a few of the rejuvenated MG samples showed compressive strain hardening. For instance, it has been reported that strain hardening can be achieved in a rejuvenated Zr-based bulk MG from the triaxially compressed notched rod region [18]. Another method is cryogenic thermal cycling, where compressive plasticity and strain hardening significantly depend on sample dimensions and cycle counts [19]. Rejuvenated MGs with improved plasticity and compressive strain hardening can be achieved through elasto-static loading and cryogenic thermal cycling, which introduce more heterogeneity on very small scales. However, the mechanism by which macroscopic MGs exhibit large ductility and strain hardening under tension has not yet been reported at room temperature. Achieving strain hardening and flow delocalization at ambient temperatures is the largest challenge in the scientific research of MGs, especially in tensile mode [7].

Strain hardening is vital for the mechanical behavior of engineering materials. It not only enhances tensile ductility but also increases flow stress and strength with plastic strain, thereby helping to prevent catastrophic failure. A significant necking phenomenon can be observed. However, inside the SB, there is always shear softening due to free volume (FV) generation and microstructure evolution in MGs. The obstacles and stoppages of SBs should counteract the strain softening and promote strain hardening. The concept of heterogeneous structure is widely accepted as a block to localized SBs. If the characteristics of the heterogeneous structure leading to a transition from strain-softening to strain-hardening behavior can be precisely tuned, then the key parameters underlying this deformation transition can be effectively identified. Since it is challenging to create MGs with strain hardening through modifications in elemental composition and microstructures during experimental procedures, theoretical simulations should precede the experiments to identify the key parameters. A dedicated study on homogeneous deformation and strain hardening is warranted through computational materials science techniques, such as molecular dynamics (MD) simulations [20–23] and finite element modeling (FEM) [24,25].

FEM is capable of addressing the aforementioned issues for length scales ranging from tens of nanometers to micrometers, which are highly relevant to experimental observations. In our previous work, we demonstrated that spatial distributions of structural parame-

ters such as the FV, especially the FV gradient interfaces, can dominate the deformation mode and shear banding. The strength and toughness can be enhanced by increasing the interface gradient [23,24]. For MGs with homogeneous spatial distributions, the statistical distributions of structural parameters influence the mechanical properties. There are two statistical parameters that one can manipulate, i.e., the mean and variance of the statistical distribution [25]. For a given mean value in MG, plasticity and toughness can be systematically enhanced with increasing statistical heterogeneity (variance), and under certain circumstances, even apparent strain hardening can be achieved. In this work, we establish finite element models that have appropriate statistical and spatial distributions of FV within the microsamples. The change in gradient structure causes a transition from strain-softening to strain-hardening behavior, as well as a transition from plastic to brittle fracturing. Then, we systematically investigate the transformation mechanisms. A deeper understanding of these transformations can guide the design and optimization of MGs with enhanced toughness and strain hardening.

2. Materials and Methods

Spatial heterogeneity in NGs, such as the introduction of second phases, local structure relaxation, or chemical change due to heavy mechanical deformation, leads to an inhomogeneous FV distribution and consequently promotes the formation of gradient interfaces [24,25]. For example, NG consists of glassy grains interconnected by loose glassy interfaces, where there are interfaces between the glassy grain and the glassy interface. As we know, networked interfaces can regulate the nucleation of multiple SBs and prevent strains from localizing within dominant SBs. The interaction between SBs and gradient interfaces warrants more attention, and their influence on deformation should be further investigated.

In the present work, we focus on exploring the interaction between the SBs and gradient interfaces and investigating the transformation mechanism of deformation modes using theoretical modelling and FEM analysis. The choice of FEM is intentional, as it enables us to match the length and time-scales of experiments, allowing for comparisons between theoretical and experimental results. The gradient interface is introduced through the initial FV spatial distribution in the samples. We focus on dealing with the gradient in one dimension across a cross-section of the sample. By distributing the specific statistical distribution of the FV, we can create a heterogeneous structure that reflects spatial patterns of gradient interfaces. The FVs are for each element following the gradient interface structures (Figure 1). The FV for each element is derived from statistical distributions obtained by transforming the beta distribution, or $0.016 \times \text{Beta}(0.1, 0.1) + 0.042$. The FVs range from 0.042 to 0.058, with a mean FV value of 0.05. The FV histogram in Figure 2 shows a symmetric bimodal distribution.

In this work, to quantitatively investigate the effect of heterogeneous microstructure on the mechanical properties of samples with varying gradient interfaces, we use an elastoplastic constitutive model that incorporates FV as an internal state variable [26–32]. The deformation strain includes both elastic and plastic strain:

$$\varepsilon_{ij} = \varepsilon_{ij}^{el} + \varepsilon_{ij}^{pl} \quad (1)$$

where ε_{ij}^{el} is the elastic strain tensor, and ε_{ij}^{pl} is the plastic strain tensor. The increment of plastic strain from the plastic flow equation is written as:

$$d\varepsilon_{ij}^{pl} = d\lambda \frac{\partial g}{\partial \sigma_{ij}} \quad (2)$$

where g is the plastic potential function based on the Drucker–Prager yield criterion, λ is the plastic deformation parameter related to FV change,

$$g(\sigma_{ij}) = b' I_1 + \sqrt{3} J_2 - K \quad (3)$$

where σ_{ij} is the Cauchy stress and I_1 is the first invariant of the stress tensor σ_{ij} , and J_2 is the second invariant of the deviatoric stress. K is a constant. The effective stress and the increment of equivalent plastic strains are expressed in the following relations:

$$\sigma_{DP} = a' I_1 + \sqrt{3} J_2 \quad (4)$$

$$d\epsilon_{eff}^{pl} = \sqrt{(2/3) d\epsilon_{ij}^{pl} d\epsilon_{ij}^{pl}} \quad (5)$$

where $a' = b'$ for the associated flow rule in the constitutive relationships. Based on the free volume theory, the plastic strain rate is a function of the FV and shear stress. The plastic strain rate and the FV change rate are presented in the following relations, respectively:

$$\dot{\epsilon}_{eff}^{pl} = 2f \exp\left(-\alpha v^* / \bar{v}_f\right) \exp\left(-\frac{\Delta G^m}{k_B T}\right) \sinh\left(\frac{\sigma_{DP} \Omega}{2k_B T}\right) \quad (6)$$

$$\frac{\partial \bar{v}_f}{\partial t} = v^* f \exp\left(-\alpha v^* / \bar{v}_f\right) \exp\left(-\frac{\Delta G^m}{k_B T}\right) \left[\frac{6\alpha k_B T(1-\mu)}{\bar{v}_f E} \left(\cosh\left(\frac{\sigma_{DP} \Omega}{2\alpha k_B T}\right) - 1 \right) - \frac{1}{n_D} + \kappa \nabla^2 \bar{v}_f \right] \quad (7)$$

where $\bar{v}_f$ is the FV value, v^* is the hard-sphere volume of the atom, Ω is the atomic volume, n_D is the number of atomic jumps needed to annihilate a free volume equal to v^* , which ranges between 3 and 10, f is the frequency of atomic vibration, α is a geometrical factor close to 1, k_B is the Boltzmann constant, ΔG^m is the activation energy, T is ambient temperature, E is Young's modulus, μ is Poisson's ratio, and κ is a free volume gradient coefficient. In the following equations, we define that $v_f = \bar{v}_f / \alpha v^*$, $S = E / (3(1-\mu)\sigma_0)$, $\sigma_0 = 2k_B T_0 / \Omega$, and $\beta = v^* / \Omega$.

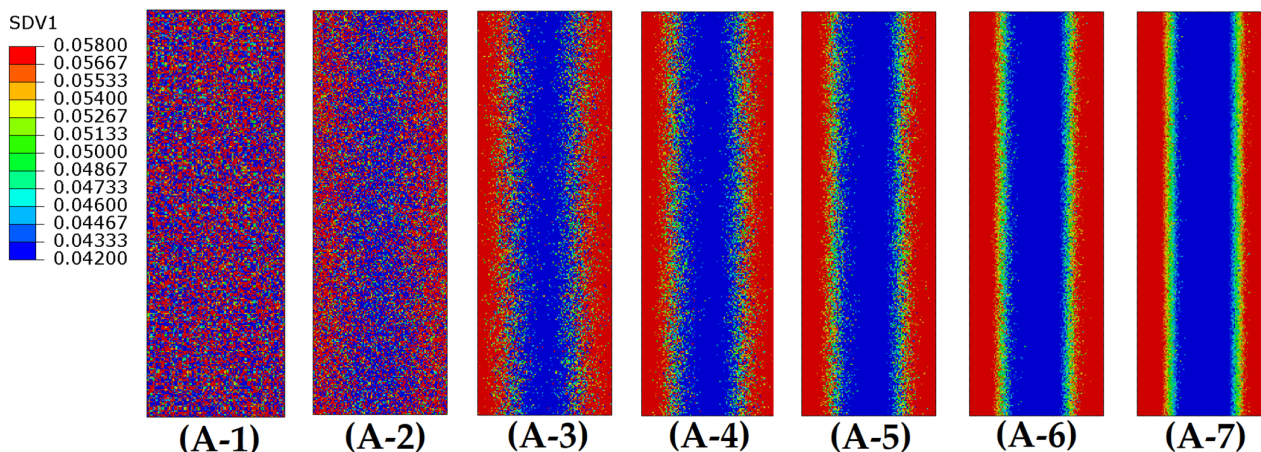


Figure 1. The initial FV spatial distributions, based on a beta function statistical distribution, are shown for seven systems (A1–A7) with varying gradient interfaces.

Equations (1)–(7) prescribe the constitutive relationship of the MG. The FV parameter, displacements, strains, and stress fields are computed using the finite element method. The displacements, strains, and stresses satisfy the governing equations:

$$\frac{\partial \sigma_{ji}}{\partial x_i} + \frac{\partial \rho v_j}{\partial t} + \rho f_j = 0 \quad (8)$$

$$\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}) \quad (9)$$

where the boundary condition is $\sigma_{ij}^* n_j = t_i$. Here, we assume that the body force f_i and the density change rate $\frac{\partial \rho}{\partial t}$ are zero. Based on the variation principle, the partial differential Equation (8) and its boundary condition are transformed into a weak form of the integral equation:

$$\int_V \sigma_{ij} \delta \varepsilon_{ij} dV + \int_{\partial V} \sigma_{ij}^* n_j \delta v_i dS = 0 \quad (10)$$

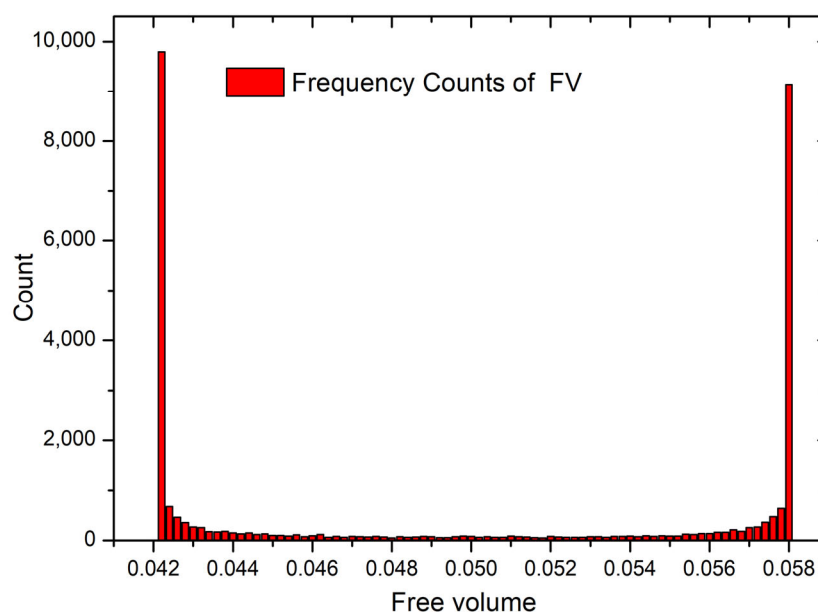


Figure 2. A histogram depicting the statistical distribution of initial FV is presented, with a range extending from 0.042 to 0.058.

The displacement field at an arbitrary location within a solid mesh element is interpolated from the values at mesh nodes through the shape function N . Substituting the interpolated shape function N into an integral Equation (10), we obtain:

$$\int_V \sigma_{ij} (\Delta \varepsilon_{kl} (u_i^a)) \frac{\partial N^a}{\partial x_j} dV + \int_V \frac{\partial \Delta \sigma_{ij}}{\partial \Delta \varepsilon_{kl}} \frac{\partial N^b}{\partial x_i} \frac{\partial N^a}{\partial x_j} \Delta u_i^a dV + \int_{\partial V} \sigma_{ij}^* n_j N^a dS = 0 \quad (11)$$

where the weak form of the integral equation is reformulated as a system of linear equations, with the size dependent on the total number of elements in FEM. The material stiffness matrix D_{ijkl}^{ep} pertaining to the constitutive relationships of MGs:

$$D_{ijkl}^{ep} = \partial \Delta \sigma_{ij} / \partial \Delta \varepsilon_{kl} \quad (12)$$

is implemented in the finite element software ABAQUS 6.13 through a UMAT subroutine [29–32]. In the implicit integration scheme, applying the backward Euler method to the flow in Equation (6) and the FV evolution in Equation (7), we obtain:

$$\sigma_{DP(n+1)}^{trial} - \sigma_{DP(n)} - \Delta \sigma_{DP} - (Kab + 3G) \frac{1}{\sqrt{\frac{2}{9}b^2 + 1}} 2\Delta t \exp\left(-\frac{1}{v_{f(n)} + \Delta v_f}\right) \exp\left(-\frac{\Delta G^m}{k_B T}\right) \sinh\left(\frac{\sigma_{DP(n)} + \Delta \sigma_{DP}}{\sigma_0}\right) = 0 \quad (13)$$

$$\Delta v_f - \frac{\Delta t}{\alpha} \exp\left(-\frac{1}{v_{f(n)} + \Delta v_f}\right) \exp\left(-\frac{\Delta G^m}{k_B T}\right) \left[\frac{1}{(v_{f(n)} + \Delta v_f) \beta S} (\cosh\left(\frac{\sigma_{DP(n)} + \Delta \sigma_{DP}}{\sigma_0}\right) - 1) - \frac{1}{n_D} + \kappa \nabla^2 v_{f(n)} \right] = 0 \quad (14)$$

In the Newton–Raphson method, the solution $(\Delta v_f^k, \Delta \sigma_{DP}^k)$ from the previous step will be used for the calculation $(\Delta v_f^{k+1}, \Delta \sigma_{DP}^{k+1})$ in the next step, and $\sigma_{DP(n+1)}^{trial}$ is the trial

stress tensor. Each plane strain model in each system has 30,000 four-node meshes, and the periodic boundary conditions are applied. All four-node plane strain elements are square, with a side length of $d = 0.1 \mu\text{m}$. The effective tensile strain rate is set at $0.1/\text{s}$ in our FEMs. By solving the system of linear equations related to the number of mesh elements, we can derive updated values for FV, displacement, strain, and stress fields. The material stiffness matrix D_{ijkl}^{ep} is also revised accordingly. The material properties of bulk $\text{Zr}_{41.25}\text{Ti}_{13.75}\text{Ni}_{10}\text{Cu}_{12.5}\text{Be}_{22.5}$ MG are used [29–32].

To obtain the mechanical properties of MG samples featuring various gradient interfaces at the microscale, we employ continuum mechanics to model the tensile behaviors of the MGs that contain the varying intrinsic interfaces. The FV distributions of systems A1–A7 are drawn from the statistical distribution, as shown in Figure 1. The initial FV profile and the corresponding FV gradient along the cross-section are shown for systems (A1–A7), with varying gradient interfaces in Figure 3. The gradients in these systems are limited by the FV statistical distributions and the number of elements in this work. In Figure 3a, system A7 has higher FV at the sides and lower FV in the center region and has a sharp interface between the high and low FV regions, while system A1 has a uniform FV spatial distribution and almost zero gradient across the sample. We can average the FV of systems along the cross-section and then differentiate the curve to obtain the FV gradient, as shown in Figure 3. In Figure 3b, average FV gradient profiles along the cross-section are shown for systems with varying gradient interfaces. One can observe that the average FV gradient along the cross-section varies. We select the maximum absolute value of the FV gradients as the characteristic parameter for the gradient interfaces, while others may choose the mean value of the FV gradient as the characteristic. In Figure 3b, the maximum absolute values of the FV gradients for all systems are as follows: $0 \mu\text{m}^{-1}$ for system A1; $0.001985 \mu\text{m}^{-1}$ for system A2; $0.005874 \mu\text{m}^{-1}$ for system A3; $0.00732 \mu\text{m}^{-1}$ for system A4; $0.00839 \mu\text{m}^{-1}$ for system A5; $0.009423 \mu\text{m}^{-1}$ for system A6; $0.00981 \mu\text{m}^{-1}$ for system A7. It is anticipated that identifying the overarching trends in strength and toughness, as well as elucidating the transition from strain-softening to strain-hardening behavior influenced by the relative differences in FV gradient interfaces, will provide critical insights into the underlying mechanisms.

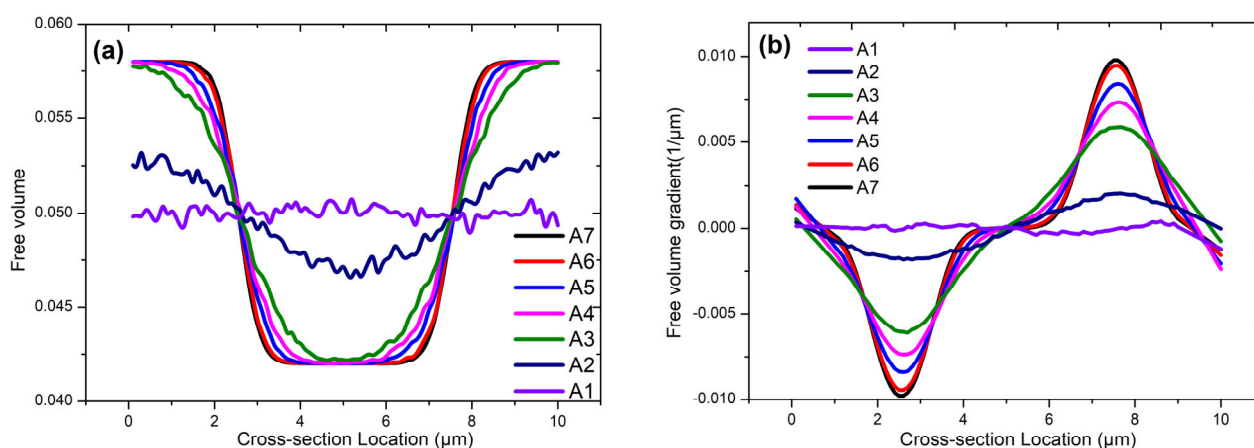


Figure 3. The initial average FV profile distributions (a) and their corresponding FV gradients (b) along the cross-section are shown for systems (A1–A7) with varying gradient interfaces.

3. Results

3.1. Mechanical Behaviors of the MGs with Varying Gradient Interfaces

The tensile stress–strain relations of systems with varying gradient interfaces are shown in Figure 4a. One can clearly see that a transition from strain-softening to strain-

hardening behavior occurs with changes in the gradient structure. System A1 exhibits strain-softening behavior after reaching its peak stress, characterized by a negative tangent modulus. Subsequently, the stress gradually decreases to a steady value as plastic strains increase. Sample A4 exhibits characteristic behavior of an ideal elastoplastic material until the stress rapidly declines to a steady value. Sample A7 exhibits significant strain hardening after the yield point, resulting in a higher peak stress or strength compared to other systems. As the strain increases in system A7, the stress reaches its peak and then rapidly drops to failure, resembling brittle fracturing behavior.

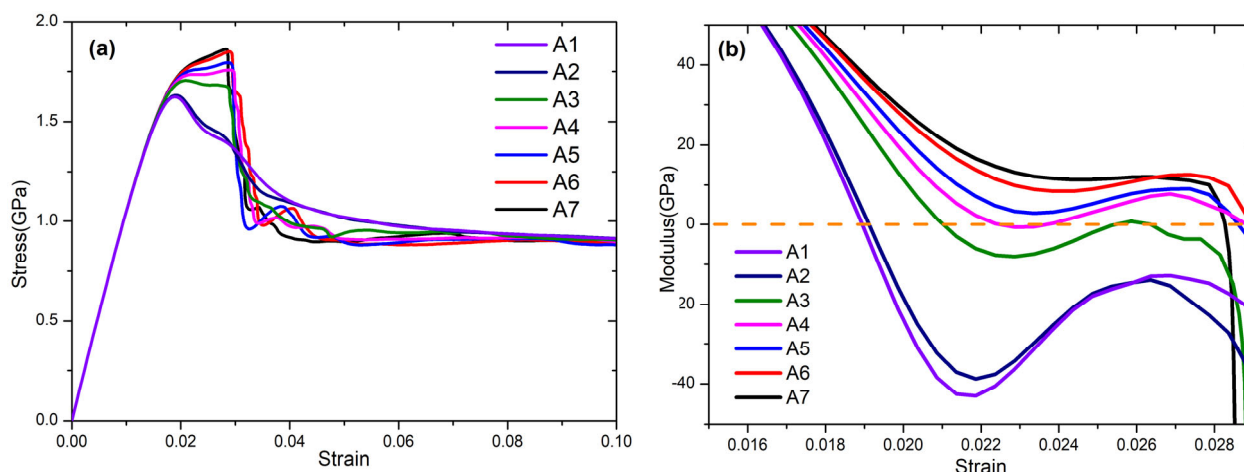


Figure 4. The stress–strain relations for systems (A1–A7) with varying gradient interfaces are shown in (a), and the tangent modulus–strain relations for the same samples are presented in (b).

Systems A1–A3 exhibit strain-softening behavior, and their peak stresses are 1.623 GPa, 1.633 GPa, and 1.705 GPa, respectively. Systems A4–A7 exhibit strain-hardening behavior, with their peak strain remaining relatively constant at approximately 2.88%. The peak stresses of systems A4–A7 are 1.758 GPa, 1.793 GPa, 1.849 GPa, and 1.861 GPa, respectively. In Figure 4b, the tangent moduli of all systems after the yield point are shown. The tangent modulus of system A7 exhibits the slowest reduction with increasing strain and remains positive prior to the peak point, whereas that of system A1 decreases the most rapidly, reaching a negative value. The mean values of the tangent moduli for all samples in the post-yield region are as follows: −43 GPa for system A1; −39 GPa for system A2; −8.1 GPa for system A3; 3.3 GPa for system A4; 6.2 GPa for system A5; 8.9 GPa for system A6; and 11.3 GPa for system A7 before the samples crack. In Figure 4b, as the strain increases, the tangent modulus decreases to zero and subsequently enters negative values, indicating the attainment of peak stress and the onset of fracture behavior, respectively. The rapid transition of the tangent modulus from positive to negative values indicates a brittle fracture, whereas a gradual progression signifies a ductile fracture.

3.2. Fracture Mode of the MGs with Varying Gradient Interfaces

The results in Figure 4a confirm our early findings that the strength and toughness can be enhanced by increasing the interface gradient. The yield stress σ_{yield} is determined using the 0.2% strain offset method. The peak stress σ_{peak} is defined as the value at which maximum stress first occurs. The steady stress σ_{steady} refers to the asymptotic stress value observed at large deformation strains; experimentally, this value is often zero due to sample cracking. For the continuum mechanics models, the sample cannot be completely sheared off; thus, the stress does not drop to zero as in the experiments. Instead, it decreases post-peak and eventually stabilizes at a constant level. In Figure 4a, the steady stress of all samples is about 0.9 GPa. We define the crack or rupture stress $\sigma_{failure}$ as the average

of the steady stress and peak stress values: $\sigma_{failure} = \frac{1}{2}(\sigma_{peak} + \sigma_{steady})$ [25]. The failure strain $\varepsilon_{failure}$ corresponding to $\sigma_{failure}$ can thus be located. The rapid decline in stress over a short strain range following the attainment of peak stress indicates brittle rupture. The fracture mode can be defined by the magnitude of the drop from peak stress to flow stress when the sample is continuously deformed following the attainment of peak stress. Here, we define the fracture mode index $\beta = (\varepsilon_{peak} - \varepsilon_{failure}) / \left(\frac{\sigma_{peak} - \sigma_{failure}}{\sigma_{failure}} \right)$ to measure the elongation per stress drop or to quantitatively evaluate the fracture mode. A larger β indicates a ductile fracture; a smaller β indicates a brittle fracture. For an ideal case of elastic–perfect–plastic material, the fracture mode index β approaches infinity, while for a perfectly brittle material, the peak stress rapidly drops to zero, allowing us to obtain $\beta = 0$.

As shown in Figure 5, the strain and stress values at the yield point, peak point, steady state, fracture point, and corresponding drop, and the fracture mode index β for different samples are summarized. In Figure 5a, the yield stress and yield strain increase as the maximum FV gradient increases. In Figure 5b, it is observed that the peak stress increases as the maximum FV gradient rises. Meanwhile, the strain corresponding to the peak stress stabilizes once the maximum FV gradient reaches a critical value, which corresponds to the structure of system A4. In Figure 5c, it is found that the steady stress remains nearly constant, indicating that it is primarily governed by the statistical distribution rather than the structural distribution. In Figure 5d, it is observed that the fracture stress increases with an elevation in the maximum FV gradient; however, the strain associated with the fracture stress remains nearly constant. To obtain the fracture mode index β , we calculate the strain drop $(\varepsilon_{peak} - \varepsilon_{failure})$ and stress drop $(\sigma_{peak} - \sigma_{failure})$, as illustrated in Figure 5e. The steady stress (shown in Figure 5c) and the strain at the fracture point (shown in Figure 5d) remain nearly constant; the stress drop is higher similar to the peak stress (shown in Figure 5b) as the FV gradient varies, whereas the strain drop (shown in Figure 5e) exhibits a trend opposite to that of the strain corresponding to the peak stress (shown in Figure 5b). The fracture mode index β is shown in Figure 5f. Variations in microstructures or FV gradient interfaces lead to a transition in the fracture mode. It can be clearly observed that the fracture mode index β decreases as the maximum FV gradient of the interface rises. Once the maximum FV gradient reaches a critical threshold, the fracture mode index β stabilizes at a constant level close to zero. In other words, the increase in the maximum FV gradient of interfaces not only alters the transition from strain-softening to strain-hardening behavior but also results in a transition from ductile to brittle fracture modes. As the maximum FV gradient approaches a significant critical value, the deformation observed in systems A5 to A7 exhibits characteristics of both strain hardening and brittle fracturing.

3.3. Effect of FV Gradient Interfaces

FV gradient interfaces in MGs and their composites are ubiquitous, occurring either naturally or as a result of artificial synthesis. The FV gradient is defined as the spatial variation of FV density in three-dimensional space. In a Cartesian coordinate system, this gradient can generally be decomposed into three orthogonal components. The spatial heterogeneity or gradient interfaces can generate a deformation gradient when subjected to directional external forces, thereby influencing microstructure evolution, deformation behavior, and fracture mechanisms. In order to simplify, our models focus on the one-dimensional gradient along the cross-sectional direction of the samples under uniaxial tension.

Typically, toughness is defined as the integral of the stress–strain curve up to the fracture point. In Figure 4a, it is evident that the integral area increases with an increase in the FV gradient, indicating improved toughness. The increasing FV gradient of interfaces facilitates a transition from strain-softening to strain-hardening behavior, as illustrated in

Figure 4a, signifying a shift from a negative tangent modulus to a positive tangent modulus. It is also observed that the strain-hardening modulus increases with an increase in the FV gradient of interfaces. In Figure 4a, following the macroscopic plastic work-hardening deformation process, system A7 rapidly transitions into a brittle fracture mode, whereas system A1 gradually shifts into a ductile fracture mode during strain softening. The transitions in the deformation modes and fracture modes should have a close relationship with the initial microstructures and their evolution; the underlying transition mechanisms will be further explored in the next section.

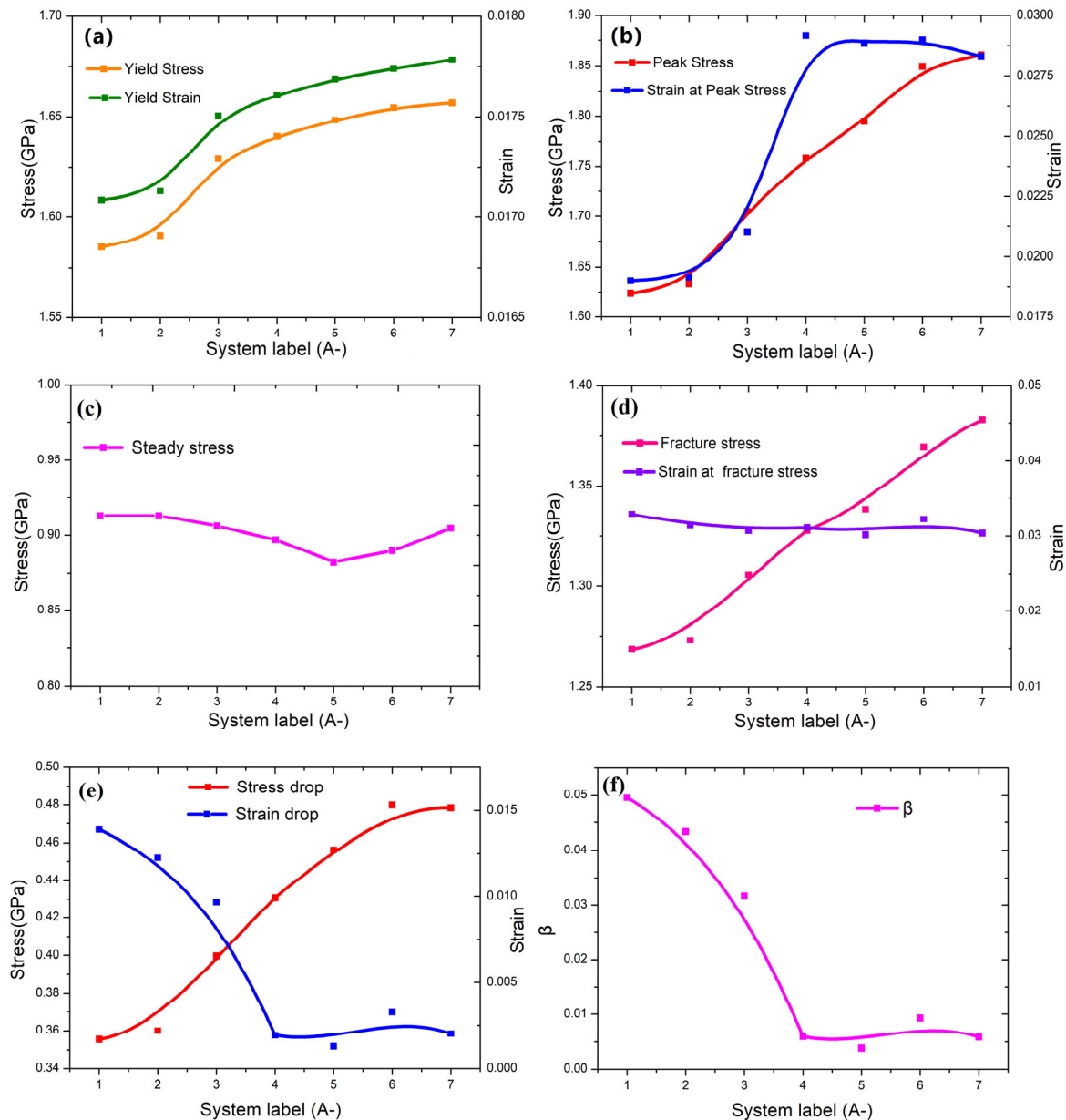


Figure 5. A summary of the stress and strain at the yield point (a), peak point (b), steady state (c), fracture point (d), and corresponding drop (e), as well as the fracture mode index β (f), for different systems (A1–A7).

4. Discussion

4.1. Transition Mechanism of Deformation Mode

The deformation mode is closely related to the initial microstructures and their subsequent evolution. To investigate the transition mechanism, we scrutinize the free volume,

shear strain, and shear stress of systems A1 (Figure 6) and A7 (Figure 7) under various representative tensile strains. In previously published experimental results, a uniform distribution of minor SBs was typically observed in ductile MGs and their composites, whereas only a few major mature SBs were present in brittle MGs [2–8,33–38]. The most natural and intuitive interpretation of this phenomenon is that controlling the initiation of shear banding and promoting a uniform distribution of the SBs can enhance the plasticity of MGs. In Figure 6, a uniform and mutually interacting distribution of the minor SBs is observed, while only a few mature SBs that traverse the entire section are shown in Figure 7.

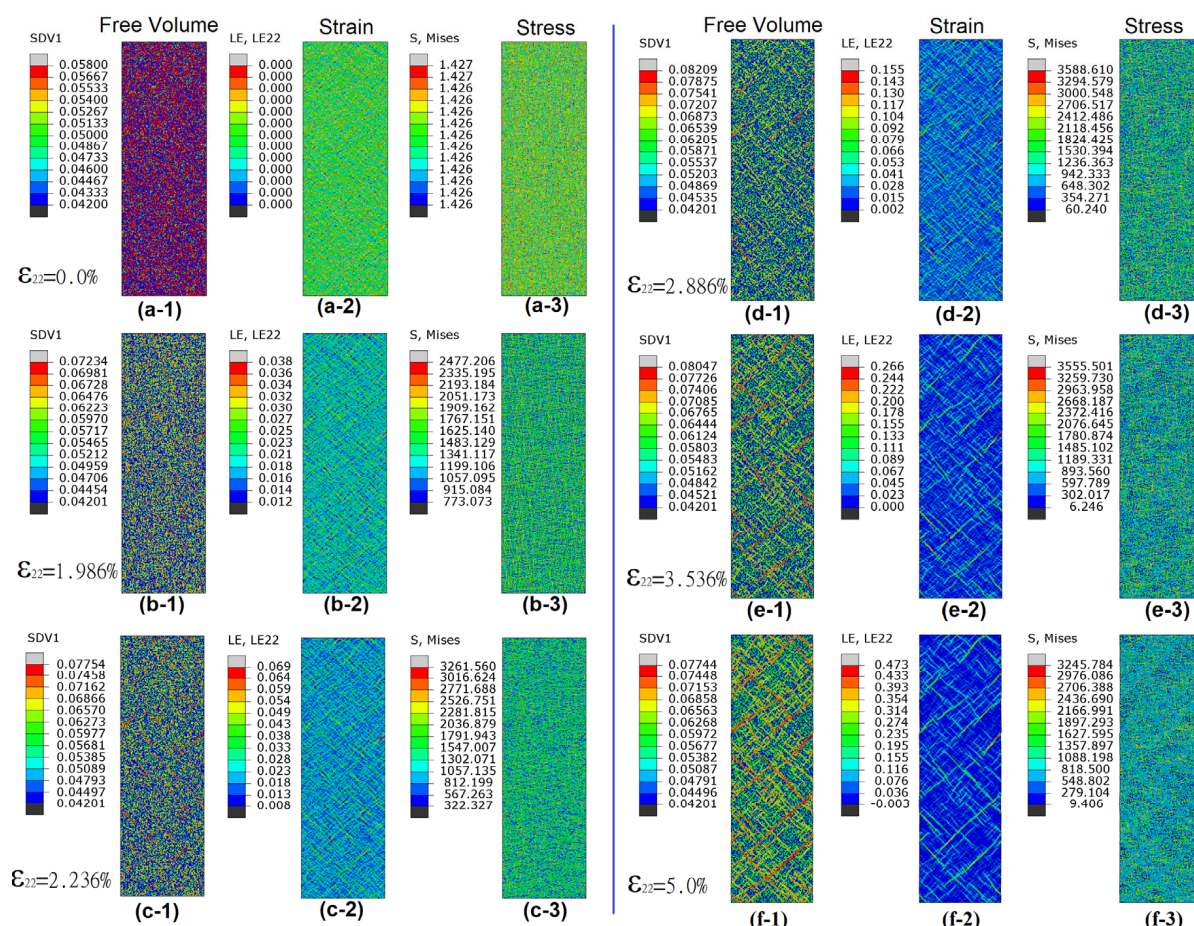


Figure 6. Contour plots for free volume (-1), shear strain (-2), and shear stress (-3) for system A1 under six representative tensile strains: (a) 0%, (b) 1.986%, (c) 2.236%, (d) 2.886%, (e) 3.536%, and (f) 5.0%. The color scheme is shown on the left of each figure.

As illustrated in Figure 6a, the initial microstructure displays a short-chain architecture characterized by an intricate interweaving of soft and hard domains. The initial deformation originating in the softer local regions remains confined to their original positions, with certain regions subsequently reaching their yield point and evolving into SB embryos, as illustrated in Figure 6b. As the deformation proceeds, the FV of certain embryos increases, thereby inducing microstructural transformation and facilitating the development of minor SBs in Figure 6c. Prior to the propagation of SBs, significant stress concentration occurs at their leading edges, leading to localized regions of high plastic strain, as shown in Figure 6d. Due to the short-chain configuration, the minor SBs within the high-FV region interact with the adjacent low-FV zone, leading to twisted and discontinuous morphologies, as depicted in Figure 6e. There is such significant strain softening within the SBs that the strain-hardening effect arising from stress concentration can no longer effectively counterbalance

it. With further deformation, the SBs remain situated in regions characterized by high strain and high FV but experience relatively low stress, as observed in Figure 6f. The short and discontinuous network-structured pathways with high FV facilitate the nucleation of multiple SBs, thereby suppressing shear localization and enhancing tensile ductility. The propagation of SBs can be arrested or bifurcated by the surrounding harder glassy chains. The enhancement in ductility is closely linked to the underlying heterogeneous microstructure and is attained at the cost of reduced strength.

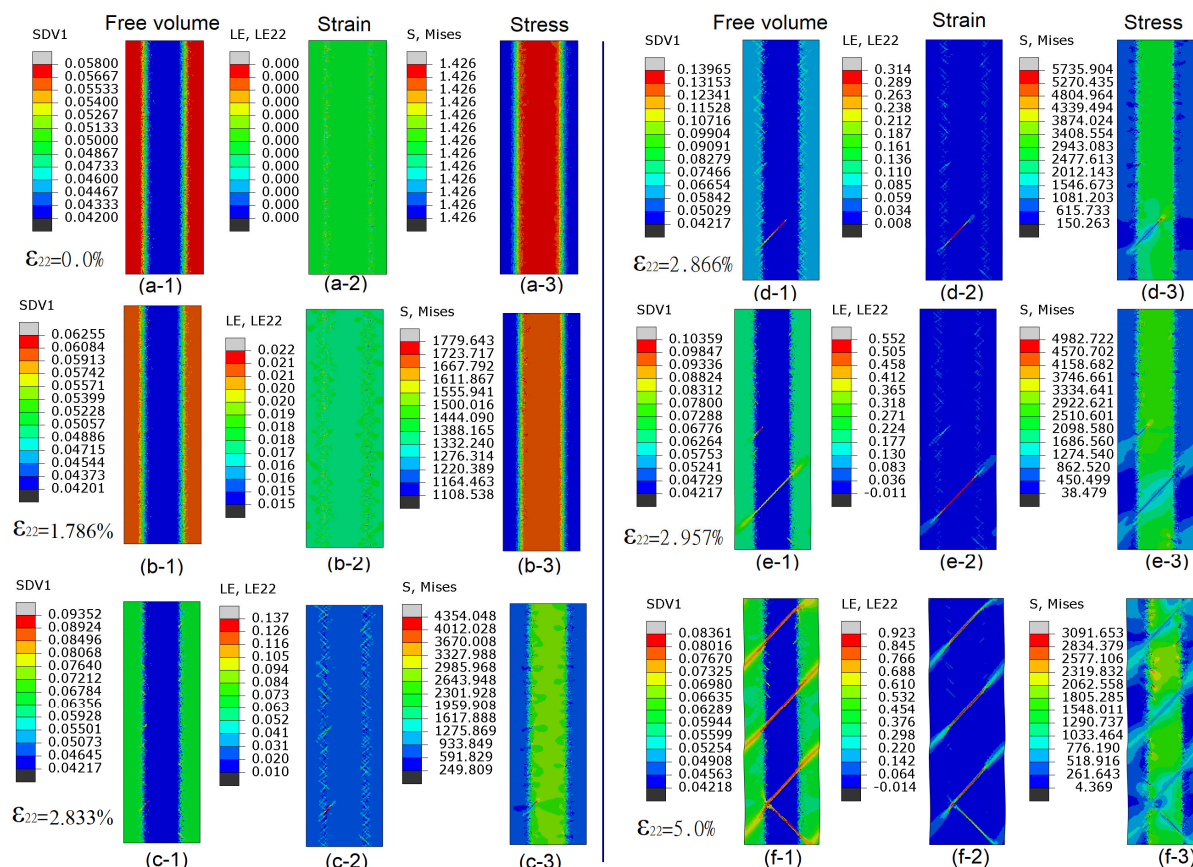


Figure 7. Contour plots for free volume (-1), shear strain (-2), and shear stress (-3) for system A7 at six representative tensile strains: (a) 0%, (b) 1.786%, (c) 2.833%, (d) 2.866%, (e) 2.957%, and (f) 5.0%. The color scheme is shown on the left of each figure.

In Figure 7a, the initial microstructure exhibits sharp interfaces that separate the regions into high FV and low FV zones. The high FV zones undergo initial deformation, accompanied by evolution in their FV or microstructure, whereas the low FV zones sustain higher stress. In Figure 7b, at a strain of 1.786%, corresponding to the yield point, the FV of the soft regions increases, whereas that of the hard regions remains nearly unchanged. As the deformation reaches the strain ($\epsilon_{22} = 2.833\%$) corresponding to the peak point, many of the stress concentrations along the serrated interfaces will form the SB embryos in Figure 7c. As the deformation continues, the SB embryos will quickly develop and grow into a major SB, which subsequently propagates through the hard zone or low FV zone in Figure 7d,e. The mature SB breaks through the interface and propagates through the sample, accompanied by a sharp drop in stress from the peak value. Under further deformation, more mature SBs cut through the sample, as in Figure 7f. It is observed that the region with low FV bears the maximum load, leading to an increase in the FV value or the evolution of the microstructure. The regeneration of new shear deformation zones is triggered by highly concentrated stress at the interface between the yield point and the peak point. The simulation results suggest that the determination of deformation modes and

behaviors should not only focus on the initiation and obstruction of SBs but also consider microstructural evolution.

To explicitly elucidate the mechanism of the deformation mode, we zoom in on the local area of initial microstructures and their evolutions. Specifically, FV profiles can be extracted along the selected cross-section, and then the FV gradient can be obtained via discrete differentiation. In Figure 8, the local microscopic FV and its corresponding FV gradient for systems A1 and A7 along a randomly selected cross-section are shown. It is observed that the maximum local microscopic FV gradient along the cross-section of system A1 is significantly larger than that of system A7, which contradicts the expected FV gradient effect. The contradictions suggest that deformation modes and mechanical behaviors should not only focus on the local microstructure or micro-morphology but also consider the characteristics of the geometrical pattern or macro-morphology, which can induce and tune the orientation of the local FV gradient. The random spatial distribution of the two-dimensional planes of samples in our models can introduce gradients exceeding one dimension, especially for system A1. The fractal dimension is a non-integer value that exceeds one. The fractal dimension of samples reflects the complexity of their microstructures. In Figure 1, the initial microstructure of system A1 exhibits a short-chain configuration, in which the soft and hard domains are intricately interwoven. The orientation of the local FV gradient will be determined by the direction of the short chain, which in turn influences the initiation and propagation of SBs. The local FV gradient orientations in system A1 are randomly distributed across all directions. The randomly distributed FV gradient orientations in system A1 yield a macroscopically uniform (i.e., non-gradient) field, whereas the regularly arranged FV distribution in system A7 generates a significant FV gradient at the macromorphological level. Similar to polycrystalline materials, the ductility and strength of a polycrystalline metal are inherently isotropic but can be influenced by the random orientation of anisotropic crystal lattices or grains.

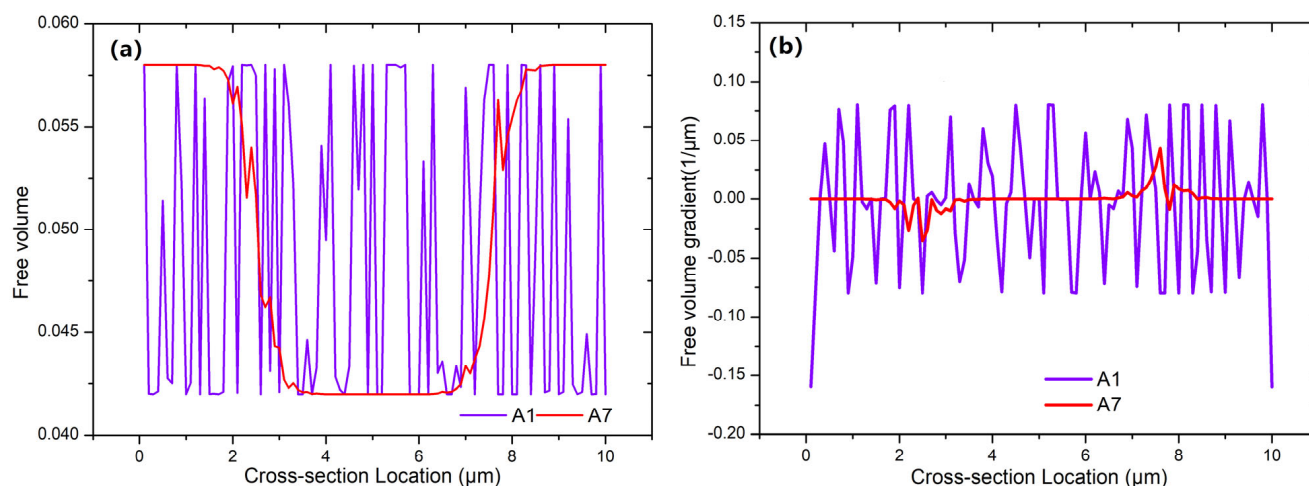


Figure 8. The local microscopic FV (a) and FV gradient (b) of systems A1 and A7 along a random cross-section are.

According to site percolation theory, the site percolation threshold represents a critical probability in statistical physics and network theory [39,40], marking the transition point at which a random system evolves from consisting of isolated clusters to forming a continuous path from one side of the sample to the opposite side. In Figure 1, the volume fraction of the red node (with high FV) in the edge zone of system A2 exceeds the percolation threshold, indicating the formation of a connected, networked structure that serves as the preferential pathway for SBs. Conversely, within the central region of system A2, the volume fraction of blue nodes (with low FV) is sufficient to establish at least one continuous

and interconnected pathway, which can effectively impede and hinder the propagation of SBs. For the structure of system A1, the random spatial distribution is extracted from the symmetric bimodal distribution. When a skewed bimodal distribution is imposed, such that either the high FV or low FV reaches the percolation threshold, it establishes an interconnected pathway that either promotes or hinders the formation of mature SBs.

Based on the Cahn–Hilliard dynamic equation, the characteristic intertwined structures progressively undergo coarsening and coalescence, resulting in spinodal decomposition that exhibits a distinct FV gradient orientation or the formation of SB channels [9,10]. The bi-continuous pattern or pathway in the microstructure of spinodal decomposed MG has a continuous angle or orientation of the FV gradient, where regions approaching the maximum resolved shear stress favor the formation of SBs. The geometry, orientation, size, and statistical and spatial distributions affecting the mechanical properties of spinodal-decomposed MG composites have been investigated [10].

4.2. Transition Mechanism of Fracture Mode

The fracture mode index $\beta = (\varepsilon_{peak} - \varepsilon_{failure}) / \left(\frac{\sigma_{peak} - \sigma_{steady}}{\sigma_{peak} + \sigma_{steady}} \right)$ exhibits a strong correlation with the steady stress, which is governed more by statistical than spatial distribution. As the steady stress increases, the index β rises. Peak stress depends on the deformation mode; strain hardening elevates it. The transition from strain-softening to strain-hardening behavior strongly influences the transition from plastic to brittle fracture. Deformation mode is tied to the initial microstructure (e.g., average FV gradient, local topology) and its evolution. The larger the FV gradient, the larger the peak stress in Figure 5b. As the peak stress increases, the index β decreases. Phenomenologically, brittle fracturing originates from the homogeneity of the sample, where a mature SB can rapidly traverse the cross-section and propagate through the entire sample, resulting in catastrophic failure. In contrast, plastic fracture arises from the distributed formation of multiple minor SBs.

To explicitly elucidate the mechanism underlying the fracture mode, we summarize the evolution of stress and microstructure or FV across the cross-section during deformation. In Figure 9a,b, contour plots illustrate the distributions of mean stress and FV along the cross-section in systems A1 and A7, respectively, under varying strain levels throughout the deformation process. In Figure 9(a-1), it is observed that prior to reaching the yield point, the stress across the cross-section increases uniformly, while the mean value of the FV remains constant, indicating a stable microstructure, as shown in Figure 9(a-2). After the peak point, the decrease in stress and the corresponding concurrent increase in FV indicate the maturation of SBs. The number of vertical stripes corresponds to the number of SBs. In Figure 9(b-1), prior to reaching the yield point ($\varepsilon_{22} = 1.786\%$), the stress across the cross-section increases uniformly, while the mean value of FV in the hard zone remains almost constant, and the FV at the interfaces adjacent to the soft zone increases very slowly. After the yield point, the stress in the hard zone increases rapidly, whereas that in the soft zone increases only gradually. The width of the interface between the hard and soft zones decreases due to the expansion of the adjacent soft zones, where the FV increases rapidly. The evolution of the interfacial structure leads to an increase in the FV gradient. As the width of the interface decreases to its minimum, system A7 reaches its peak state ($\varepsilon_{22} = 2.833\%$). The SB embryos in the hard zone begin to nucleate and grow, driven by stress concentration, thereby promoting their propagation. Due to the homogeneity of the hard zone, the SBs rapidly develop and propagate across it without encountering any significant resistance. Following the peak point, the stresses in both the hard and soft zones rapidly decrease and subsequently stabilize at their steady-state stress levels.

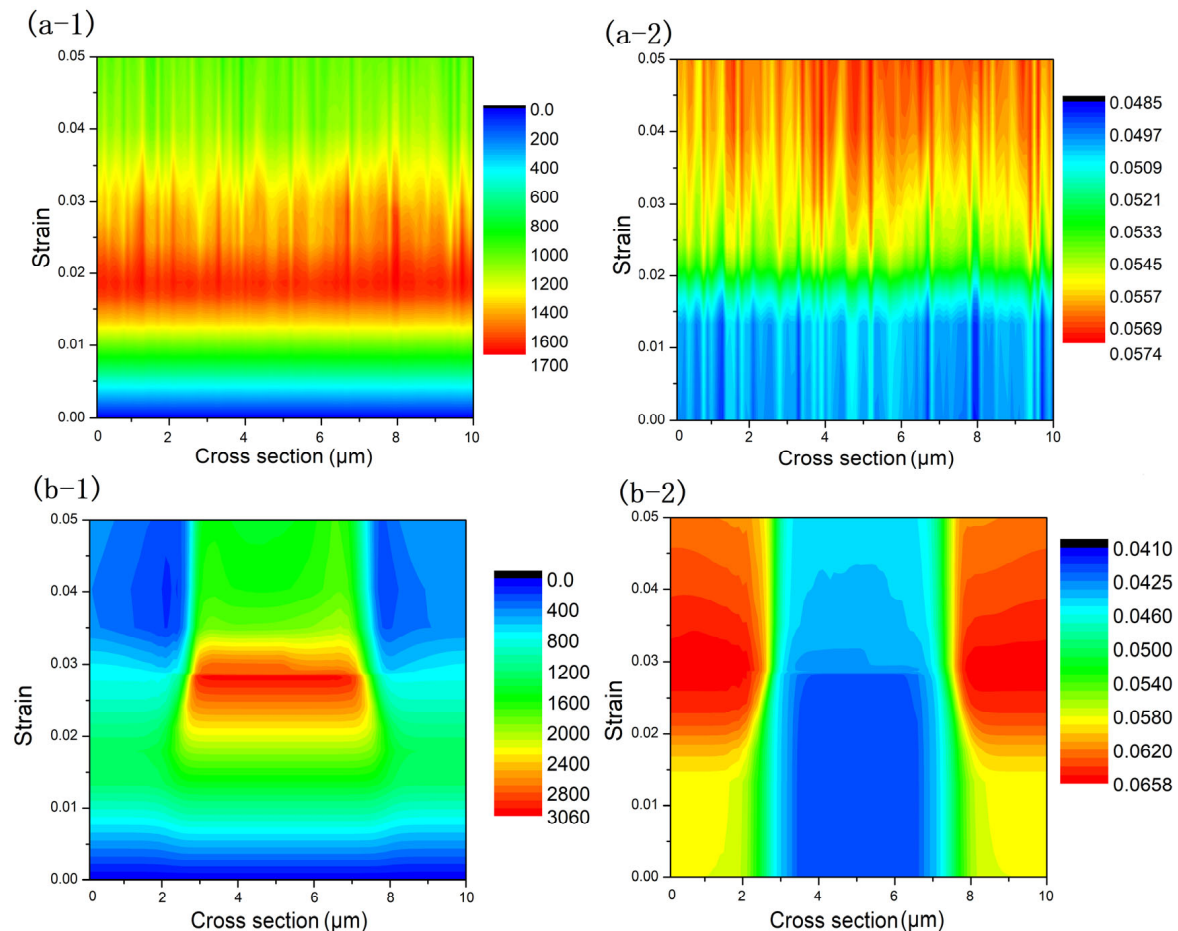


Figure 9. The contour plots of the mean value of stress (-1) and FV (-2) of system A1 (a) and A7 (b) at varying strains during the deformation.

In our simulations, the FV is designated as a structural parameter. In Figure 10a, the average FV of samples (systems A1 to A7) with varying gradient interfaces under tension is presented. The average FV values of all samples slightly decrease before 1% strain, then rise rapidly. System A1 exhibits the most rapid increase in FV value, whereas A7 shows the slowest. At the peak strain ($\epsilon_{22} = 2.833\%$), the second increase in the FV value observed in system A7 corresponds to the propagation of the major SB; after the boost, the FV gradually decreases and eventually stabilizes at a constant level. In contrast, the FV of system A1 exhibits a gradual increase following the fracture point. In Figure 10b, the FV change in the soft and hard zones during deformation is plotted. The FV value in the hard zone gradually increases under primary loading prior to the peak point, indicating microstructural evolution within the hard zone and resulting in strain hardening. The three distinct spikes in FV within the hard zone correspond to the three major SBs intersecting the section. After SBs propagate through the sample, the FV within the hard zone increases, whereas that in the soft zone decreases.

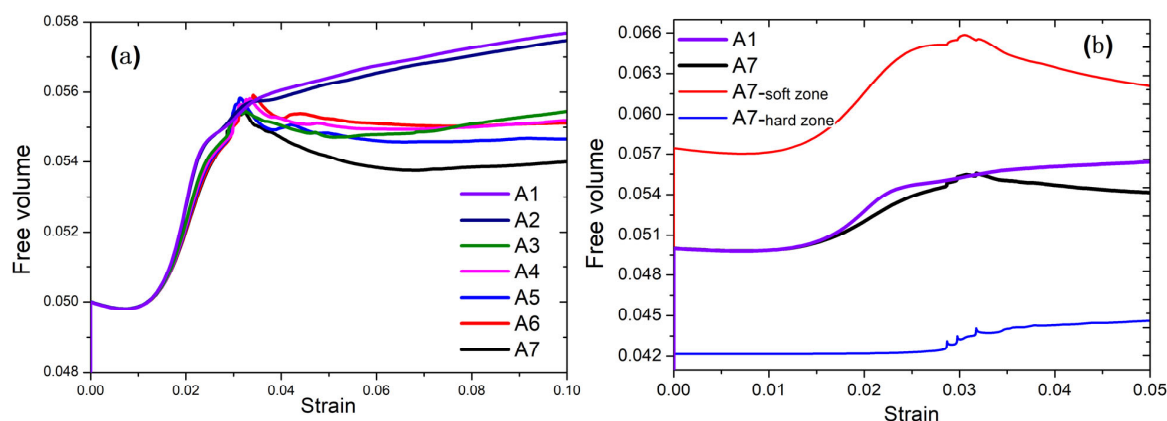


Figure 10. The average mesoscopic FV of systems (A1–A7) with varying gradient interfaces under tension is shown in (a). The average mesoscopic FV for the soft and hard zone in system A7 is shown (b), along with a comparison to systems A1 and A7.

5. Conclusions

In conclusion, we performed systematic numeric modeling using FEM in conjunction with the constitutive model that explicitly incorporates the FV variation to investigate the influence of varying FV gradients on the overall mechanical properties. In this work, we select appropriate statistical distributions of FV and FV gradient structures, and systematically investigate the transition mechanism on the deformation mode and fracture modes, which have a close relationship with the initial microstructure and its evolution. The deformation mode is determined by the comprehensive competition between the strain softening within the SBs and the strain-hardening effect induced by stress concentration at the FV gradient interfaces, which can impede the propagation of SBs [33–38,41–48]. The local short-chain structure with high FV, aligned along the direction of maximum resolved shear stress, can effectively promote local shear deformation and initiate the formation of SB embryos in a randomly distributed spatial morphology. During the deformation, the reduction in width of the gradient interfaces results in an increased FV gradient within the regularly distributed spatial morphology. The FV gradient interface along the tensile direction can effectively impede the propagation of SBs, leading to stress concentration and thereby enhancing the strength or second strain-hardening modulus.

Here, we define the fracture mode index β to quantitatively characterize different fracture modes: a lower index indicates brittle fracturing, whereas a higher index signifies plastic fracturing. The maximum gradients of samples 1 to 7 increase progressively in Figure 3b. As shown in Figure 5f, for a given statistical distribution, the larger the FV gradient, the smaller the fracture mode index β . When the FV gradient reaches a critical threshold, the fracture mode index β reaches zero and remains constant thereafter, indicating that an excessively large FV gradient promotes brittle fracture behavior. The mean tangent moduli of all systems after the yield point increase with the FV gradient. A large FV gradient enhances strain-hardening behavior and raises the peak stress. Based on the definition of the fracture mode index β , the transition from strain-softening to strain-hardening behavior strongly influences the transition from plastic to brittle fracturing.

Phenomenologically, brittle fracturing originates from the homogeneity of the sample, where a mature SB can rapidly traverse the cross-section and propagate through the entire sample, resulting in catastrophic failure. In contrast, plastic fracturing arises from the distributed formation of multiple minor SBs. In other words, strain-softening can alleviate or adjust the brittle fracture mode. A deeper understanding of these transformations can help design and optimize MGs for enhanced toughness and strain hardening. The fracture mode index is closely related to the steady stress, which is primarily influenced by the

statistical distribution more than the spatial distribution. As the steady stress increases, the index rises. For strain softening, the increased steady stress leads to an ideal elastic–plastic behavior; for strain hardening, it induces a second strain-hardening behavior and plastic fracturing. We should pay more attention to skewed bimodal distributions. Another way to achieve ideal elastic–plastic behavior is to reduce peak stress to steady stress by engineering specific structural patterns or microarchitectures, such as the bi-continuous network inherent from spinodal decomposition or networked interfaces in NG. For spatial structures, the multi-scale heterogeneous structure or morphology—characterized by high FV short-chain domains encapsulated within regions of low FV—enables the initiation and formation of SBs upon reaching a critical size. Meanwhile, the presence of hard domains constrains the propagation of these SBs and counteracts the strain-softening behavior, thereby enhancing their strength and strain hardening. Furthermore, the hierarchical interfaces effectively impede the catastrophic extension of SBs and suppress the development of brittle fractures.

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