Sarac, B.; Klusemann, B.; Xiao, T.; Bargmann, S.:

Materials by design: An experimental and computational investigation on the microanatomy arrangement of porous metallic glasses

In: Acta Materialia (2014) Elsevier

DOI: 10.1016/j.actamat.2014.05.053

Materials by design: an experimental and computational investigation on the microanatomy arrangement of porous metallic glasses

Baran Sarac [1*], Benjamin Klusemann[2], Tao Xiao[1], Swantje Bargmann[1, 2]

[1] Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Max-Planck Str. 1, 21502 Geesthacht, Germany

[2] Institute of Continuum and Material Mechanics, Hamburg University of Technology, Eissendorfer Str. 42, 21073, Hamburg, Germany

Keywords: bulk metallic glass, porous material, finite element modeling, mechanical testing, continuum mechanics

* Corresponding author

The correlation of a material's structure with its properties is one of the important unresolved issues in materials science research. This paper discusses a novel experimental and computational approach by which influence of the pores on mechanical properties of bulk metallic glasses (BMGs) can be systematically and quantitatively analyzed. The experimental stage involves the template fabrication whose pore configurations are predetermined by computer aided design tools, and replication of the designed patterns with bulk metallic glasses. Quasi-static mechanical characterization of these complex microstructures is conducted under uniaxial tension and in-plane compression. For the numerical simulations, we establish a non-local gradient-enhanced continuum mechanical model using thermodynamic principles and periodic boundary conditions. The combination of the experimental and numerical results has identified the importance of the pore configuration, overall porosity, and diameter to spacing ratio of the pores to attain optimized material properties.

1. Introduction

Advanced microstructures with desirable properties have long been an interest of material

scientists to investigate the relationship between material's internal structure and its physical properties, such as strength, flexibility and durability. This holds true for various materials; in this contribution we focus on metallic glasses – an amorphous solid which is stronger than its crystalline counterpart but usually also brittle. One important task is to design metallic glasses optimized for tensile ductility.

Today's state-of-the-art is not conforming to the needs of the current technology to decipher the microstructural complexity due to the multi-scale nature of advanced alloy systems determined by undercooling [1, 2]. An important barrier is imposed by the fabrication techniques, where the strong network between different second phase parameters (i.e., density, size, shape, dispersion of second phases, and residual stress distribution over the sample) does not permit to construct the targeted microstructure, and thereby achieve the desired material properties.

Bulk metallic glasses (BMGs) possess an exclusive combination of very high fracture strength and strain as well as extensive elasticity [3-7], along with their thermoplastic processability [8, 9]. These favorable material characteristics emerge from the absence of grain boundaries and dislocations in the glassy state, which permits the deformation to evolve isotropically. Furthermore, it has previously been suggested through experiments and observations that shear band localization in bulk metallic glass heterostructures alters the mode of deformation and enables controlled shear development as long as the spacing between the second phase features is equal or smaller than the critical crack length of the sample [10-12]. This effect is more pronounced under uniaxial compressive deformation, where multiple shear band activation between the second phase particles remarkably enhances the mechanical response [13-16]. Yet, what was essentially missing in this puzzle is the quantitative assessment of the influence of each second phase feature on mechanical behavior. A novel study has addressed this drawback by arranging the microanatomy of engineering materials using a two-step fabrication technique and analyzing heterostructures (systems with more than one phase, i.e., pores as second phase) described in [17-19], where the influence of parameters on structural properties can be individually traced.

Computational methods such as molecular dynamics simulations [20-26], jammed granular matter [27, 28], Bernal's hard sphere model [29, 30] or colloidal systems [31-34] have been employed to analyze the atomic packing and free volume creation, which is particularly useful

for analyzing the deformation mechanism at the nano-scale. However, the findings based on the atomic-colloidal interactions and the other pursued methods impose a challenge when the entire sample size is orders of magnitude bigger than the characteristic feature size. This limitation is accounted by the representative volume element selected or inaccurate representation of kinetics in computational systems, which limits the applicability of this technique on wider length-scales. On the other hand, classical continuum mechanics approaches have been introduced to study the size dependency of metallic glasses using finite element methods [35-39], where they provide significant advantages in terms of simulation time and system size compared to the corresponding experimental methods. Nevertheless, these material models are either not considering non-local stress distributions or showing deviations from the actual response at large deformations due to local truncation errors of the numerical approximation.

Thamburaja [38] presented one of the first approaches in which an explicit model can be implemented to capture the deformation behavior of nanometric sized samples. In the recent works of Bargmann et al. [40, 41], size effects in metallic glasses have been investigated based on a gradient enhanced, energy-based mathematical model. The model is formulated thermodynamically consistent, and captures important physical aspects such as free volume generation, shear localization, and fracture mechanism in small-sized metallic glasses. Moreover, the finite-deformation based theories can be utilized to monitor the influence of intrinsic material length scale on feature sizes through shear band development and arrest in multi-phase systems.

A critical limitation for an experimental study occurs when the thickness of the sample is one order of magnitude smaller than the other dimensions, which is mainly imposed by the maximum depth of the silicon templates achievable with the anisotropic etching through conventional lithography, as well as the flow kinematics of the viscous metallic glass in its supercooled region. This limitation is also reflected on in-plane compression tests with circular pores, where samples with low porosity (e.g., $P \leq 30\%$) are challenged by out-of-plane deformation caused by the Euler buckling instability, which prevails before the structures reach their yield strength [19]. To this extent, numerical analysis of the metallic glass heterostructure under plane-strain conditions brings an advantage and accuracy over the previously pursued experimental study by eliminating the out-of-buckling problem.

In this work, we benefit from the aforementioned non-local energy-based mathematical

model to investigate the size effect in metallic glasses under in-plane compression. A variety of metallic glass heterostructures having different porosities and pore configurations are numerically analyzed within a finite element framework. In addition, the numerical results are integrated with the experimental studies of these periodic heterostructures of whose quantitative parameter investigations are simultaneously conducted.

2. Experimental Background

Throughout this paper, $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ BMG alloy is utilized, which possesses high strength of 1430 MPa under compression, comparable density with light metals, and entensive processing window of ~160 K [18, 42]. The considered attributes confer excellent thermoplastic processability to the selected alloy, which allows for precise micro-replication of highly complicated shapes [43, 44]. Second phase features with significantly smaller radius of curvature (e.g., oval pores or pores with sharp edges) are found to be deteriorating the mechanical properties due to the fact that the stress concentration generally accumulates at the sharp tips, causing the material to break along a single shear band (as previously discussed in [19, 45]). For this reason, the shape of the pores is selected to be circular in both experimental and numerical studies, which provides the most uniform stress distribution throughout the sample.

A selection of experimental specimens for uniaxial tension and in-plane compression are fabricated by using a two-step production method, where the templates out of silicon wafer are created by the conventional lithography. The templates are subsequently imprinted to the metallic glass using the concept of thermoplastic forming (Fig. 1a). The prepressed $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ BMG disc with a thickness of ~1 mm was filled into the template at 700 K for 1 min under an applied pressure of 50 MPa. The low viscosity at this processing temperature ($\eta = 10^6$ Pa s) with a calculated lateral flow stress of around 0.3 MPa (assuming Newtonian flow behavior $\sigma = 3\eta\dot{\varepsilon}$ and quasi-static conditions $\dot{\varepsilon} = 10^{-1}$) accommodates template replication with convenience and precision. The surfaces of replicated samples are at first grinded and polished to establish a fine surface smoothness. The samples are then taken out of the mold by chemical etching using a diluted KOH (35% by mass) solution. The surface textures of the templates (submicron roughness generated due to sequential chemical etch) are

replicated almost exactly with the same precision due to the material's intrinsic flow characteristics discussed above.

Quasi-static in-plane compression and uniaxial tension tests are conducted using Instron mechanical testing machine. Compression test setup includes a pair of steel molds for the top grip, a steel mold and a glass panel for the bottom, and shim steels acting as plunger (top) and a base plate (bottom) (Fig. 1b). The heterostructures with circle-like pores have periodically stacked hexagons with filleted inner corners. The radius of the corner-fillets (r) has been selected based on the ligament thickness (t), where r/t ratio is kept constant as 0.3 (see [18]). The structure is standing on the base plate bolted between the steel mold and glass panel, where the in-plane compression is established by the top plunger clamped between the top steel molds. Custom-made stainless steel pneumatic compartments are utilized to eliminate slippage and misalignment between the top and bottom parts. Alumina piece is placed behind the structure to increase the contrast during in-situ imaging, as well as to minimize the friction between the structure and the surface during deformation. The quasi-static in-plane compression is performed by the compression of the top plunger, where the size of the shim steel is thicker than the structure to establish a uniform deformation and prevent self-buckling. For the tensile test, the samples with the pattern of periodically spaced circular pores are at first imprinted to the gauge section of the specimen. The fabricated heterostructure is subsequently pinned from their grip sections to the pair of steel plates on each side. The pins provide uniform stress transfer to the samples throughout the test, as well as eliminate undesired stress localizations on the other parts of the specimen before the actual deformation in the gauge section proceeds (Fig. 1c). In both deformation types, in-situ examination of the deformation behavior is performed by an optical microscope with high depth of field and resolution to control the test precision.

Fig. 2 shows the templates of the compression and tensile heterostructures, and the replicated metallic glass samples out of these templates. The combination of computer aided design and photolithographic template fabrication has high versatility and throughput, yielding tens of samples with different designs from the same silicon wafer at second phase feature precision. More details regarding the sample fabrication and final precision, as well as the mechanical characterization setup and test protocol can be found in [17-19].

Figure 1 – (a) Experimental samples are fabricated through the combination of

photolithography and thermoplastic forming. Test setup of (b) compression heterostructures with circle-like pores and (c) tensile heterostructures with circular pores, where both tests are conducted under quasi-static conditions $\dot{\varepsilon} = 5\ x\ 10^{-3}\ s^{-1}$.

Figure 2 –Bulk metallic glass test samples and the scale-up images of the microfeatures (indicated by arrows). (a) Tensile heterostructure with periodically spaced circular pores. (b) Compression heterostructure with periodically spaced circle-like pores. The dimensions of the scales (in black) below the fabricated structures are (a) 1 mm and (b) 250 μm, respectively. The blue scales for inset images are (a) 100 μm and (b) 500 μm, respectively. The thickness (or the filling depth of the Si wafer) of the samples are one order-of-magnitude smaller (~300 μm) than the entire width and height.

3. Mathematical Model

Kinematics of the large strain continuum mechanical model involves several important notations need to be discussed. To start with, the plastic deformation is assumed to be irrotational for amorphous materials, i.e., $\boldsymbol{W}_b = 0$ [46].The rate of change in plastic stretching tensor is calculated from the spherical and deviatoric (traceless) parts given by:

$$\boldsymbol{D}_{\mathrm{P}} = sph(\boldsymbol{D}_{\mathrm{P}}) + dev(\boldsymbol{D}_{\mathrm{P}}) = \frac{1}{3} tr(\boldsymbol{D}_{\mathrm{P}})\boldsymbol{I} + \sqrt{\frac{1}{2}}\dot{\gamma}\boldsymbol{N}\ , \qquad (1)$$

where $\boldsymbol{I}$ and $\boldsymbol{N}$ are the identity matrix and the deviatoric unit vector in the plastic flow direction, respectively. Here, we define the equivalent shear stress by $\bar{\tau} = \sqrt{\frac{1}{2}}|dev(\boldsymbol{M})|$ and the hydrostatic pressure by $\bar{p} = -\frac{1}{3} tr\boldsymbol{M}$ in terms of Mandel stress $\boldsymbol{M}$. The spherical part of the deformation represents the deformation due to the free-volume generation with $tr(\boldsymbol{D}_{\mathrm{P}}) = \dot{\xi}$, whereas the deviatoric component exhibits the movement of atomic clusters due to shear [47]. The elastic part of the deformation is denoted by the elastic right Cauchy-Green deformation $\boldsymbol{C}_{\mathrm{e}} = \boldsymbol{F}_{\mathrm{e}}^{\mathrm{T}} \cdot \boldsymbol{F}_{\mathrm{e}}$ and elastic Green-Lagrange strain tensors $\boldsymbol{E}_{\mathrm{e}} = \frac{1}{2}[\boldsymbol{C}_{\mathrm{e}} - \boldsymbol{I}]$. The multiplication of the plastic and elastic components of the deformation gradient results in the deformation of the total body at large strains $\boldsymbol{F} = \boldsymbol{F}_{\mathrm{e}} \cdot \boldsymbol{F}_{\mathrm{P}}$.

The total free volume generation within the heterostructure arises from the plastic shearing (constitutes the first part of Eq. (2)), as well as from other mechanisms (denoted by $\dot{\xi}_{\mathrm{m}}$) such as

diffusion, hydrostatic stress or structural relaxation [48, 49]:

$$\dot{\xi} = s_\gamma \dot{\gamma} + \dot{\xi}_\mathrm{m} \,. \tag{2}$$

A thermodynamically consistent theory is formulated in [40] as a function of the plastic component and total deformation gradients ($\boldsymbol{F}_\mathrm{P}$ and $\boldsymbol{F}$ respectively), plastic strain γ, free volume ξ, and gradient of free volume $\nabla_{\boldsymbol{X}}\xi$, where the free energy is partitioned into hyperelastic, defect and gradient components:

$$\Psi_0\left(\boldsymbol{F}, \boldsymbol{F}_{\mathrm{P},} \gamma, \xi, \nabla_{\boldsymbol{X}}\xi\right) = \frac{\mu}{2}[\boldsymbol{C}_\mathrm{e} - \boldsymbol{I}]\colon \boldsymbol{I} + \frac{\lambda}{2}\ln^2 J_\mathrm{e} - \mu \ln J_\mathrm{e} + \frac{1}{2}a_\mathrm{def}\xi^2 - a_\mathrm{def}\xi\xi_0 + \frac{1}{2}a_\mathrm{sf} l [\nabla_{\boldsymbol{X}}\xi]^2 \tag{3}$$

In this equation, λ and μ are the Lamé parameters for the elastic part and J_e= $\det \boldsymbol{F}_\mathrm{e}$ is the elastic Jacobian. Furthermore, dissipative kinetic processes are expressed via the dissipation potential χ in two parts related to plastic strain (Eq. (4) left term) and to all other mechanisms for free volume generation (Eq. (4) right term):

$$\chi = \frac{\dot{\gamma}_0 n}{n+1} c \left[\frac{\dot{\gamma}}{\dot{\gamma}_0}\right]^{1/n+1} + \frac{1}{2}\frac{a_\mathrm{res}}{v_\mathrm{m}}\dot{\xi}_\mathrm{m}^2 \,. \tag{4}$$

The formulation of the material model includes energy-based constitutive equations to identify the effect of shear localization, as well as the internal length scale on the overall deformation mechanism. The cohesion c, plastic strain γ and free volume ξ are governed by rate-dependent evolution equations [40, 41]:

$$\dot{c} = c\frac{b\dot{\xi}}{\cosh\left(\frac{\dot{\xi}}{v_0 \exp\left(-\frac{Q}{k_\mathrm{b}\theta_0}\right)}\right)} \,, \tag{5}$$

$$\dot{\gamma} = \dot{\gamma}_0 \left[\frac{\bar{\tau} - s_\gamma\left[\bar{p} + a_\mathrm{def}[\xi - \xi_0]\right] + s_\gamma a_\mathrm{sf} l \mathrm{Div}(\nabla_{\boldsymbol{X}}\xi)}{c}\right]^n \,, \tag{6}$$

$$\dot{\xi} = s_\gamma \dot{\gamma} + \left[v_\mathrm{m}\frac{l\, a_\mathrm{sf}}{a_\mathrm{res}}\right]\mathrm{Div}(\nabla_{\boldsymbol{X}}\xi) - \frac{v_\mathrm{m}}{a_\mathrm{res}}\left[\bar{p} + a_\mathrm{def}\,[\xi - \xi_0]\right] \,. \tag{7}$$

Here, b denotes a fitting constant, v_0 frequency of the atomic vibration, Q the activation energy, k_b the Boltzmann constant. Eq. (7) consists of the viscous-like and non-local back stress terms represented by $p + a_{def}[\xi - \xi_0]$ and $a_\mathrm{sf} l \mathrm{Div}(\nabla_{\boldsymbol{X}}\xi)$, respectively. The diffusion

coefficient in eq. (7) is expressed by $\frac{\upsilon_{\mathrm{m}} a_{\mathrm{sf}}}{a_{\mathrm{res}}}$. The free volume generation $s_{\gamma}\dot{\gamma}$ and annihilation $\frac{\upsilon_{\mathrm{m}}}{a_{\mathrm{res}}}\left[\bar{p} + a_{\mathrm{def}}\left[\xi - \xi_0\right]\right]$ terms contribute to the free volume content of the heterostructure as deformation is proceeding. The frequency like term $\upsilon_{\mathrm{m}} = \upsilon_0 \exp\left(-\frac{Q}{k_{\mathrm{b}}\theta_0}\right)\sqrt{\exp(-\phi/\xi)}$ introduces the thermal activation component into the model. ϕ is a dimensional fitting constant varying between 0.1 and 1 [50, 51].

The material parameters are given below at room temperature (see Table 1). The Young's modulus and the Poisson's ratio values for $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ are provided in Duan et al. [42]. Fully annealed free volume parameter ξ_0 is taken from [47], fracture surface energy a_{sf} from [52], and defect-free energy coefficient a_{def} and resistance to free volume generation due to mechanisms other than plastic strain a_{res} from [53]. The coupling parameter s_{γ}, strain rate sensitivity n, initial cohesion c_0, material strain rate $\dot{\gamma}_0$ (quasi-static deformation) are adopted from [41].

Parameter	**Symbol**	**Value**
Young's Modulus (monolithic)	E	86.9 [GPa]
Poisson's Ratio	ν	0.37 [-]
Coupling Parameter	s_{γ}	0.02 [-]
Resistance to free volume generation	a_{res}	320 [GJ/m^3]
Defect free energy coefficient	a_{def}	3500 [GJ/m^3]
Fracture surface energy	a_{sf}	1 [J/m^2]
Plastic process zone size	l	100 [µm]
Strain rate sensitivity	n	50 [-]
Fully annealed free volume	ξ_0	0.09 [%]
Initial cohesion	c_0	750 [MPa]
Macroscopic strain rate	$\dot{\gamma}_0$	0.005 [s^{-1}]

Table 1 – Material properties adopted for the mathematical model.

Using the basic fracture mechanics equation derived for BMGs [54], the measured plastic zone size (or in other words, the critical crack length l) of the considered metallic glass type is

determined to be ~100μm. Macroscopic strain rate of 0.005 s^{-1} is chosen to satisfy the quasi-static loading and to match the strain rate of the experimental study. Furthermore, $\phi = 0.2$, $b = -300$ and $v_0 = 327\ s^{-1}$ [50, 51, 55].

4. Numerical Investigation of Metallic Glass Heterostructures

4.1 Finite Element Solution Strategy

The solution strategy is based on a dual mixed finite element algorithm (e.g. [56]). The pursued method provides solution for the plastic strain γ and free volume ξ in the Gauss points, whereas nodal values are calculated for the displacement $\boldsymbol{u}$ and the free volume gradient $\boldsymbol{h} = \nabla_{\boldsymbol{X}}\xi$. Micro-free boundary conditions ($\boldsymbol{h} \cdot \boldsymbol{n} = 0$) are applied to the free volume. Periodic boundary conditions are pursued to investigate the response of a representative volume element. This method has significant advantages over fixed-end boundary conditions by eliminating the surface effect on the deformation mechanism, and provides correct estimations of mechanical properties for finite volume analysis in large systems (i.e. micro/macroscopic level). For the convenience of the numerical approximation, the samples are discretized into 1500 to 2250 plane-strain elements depending on the pore configurations. Furthermore, to ensure an asymmetric deformation at the beginning of the plastic deformation, a local defect is generated by assigning 2% lower cohesion value to an element in the near vicinity of the pore located in the middle of the sample.

4.2 Influence of Microstructural Configuration

At first, we look at two dimensional periodic heterostructures of different pore configurations. In this regard, the experimental data of Sarac and Schroers [17] have revealed that the porosity and pore configuration in metallic glass heterostructures plays an important role for enhancing the overall deformation mechanism, which are accounted for enhancing the elasticity of the sample through the stretching of the material parts between the pores. To maximize the effect of stretching, the pores are located in a way that the center of the pore is coinciding with the midpoint of the neighboring stack, namely as AB pore configuration. Fig. 3a shows the sketches of material geometries confined between the different stacks of pores.

All samples with circular pores of 20% porosity have fixed pore diameters of 50 μm. Fig. 3b

has an AB pore stacking with constant spacing of 50 μm between the pores in the lateral direction (sample I). AB pore stacking with constant spacing of 50 μm between the rows of each AB stack (sample II) is illustrated in Fig. 3c, whereas Fig. 3d includes pores with AA pore stacking with constant spacing of 50 μm between the pores in the lateral and vertical directions (sample III). To establish periodic translation symmetry, the initial width of the entire sample is fixed to be 400 μm, where the initial height is 400 μm for samples I and III, and 450 μm for sample II.

The simulation results and the correlated stress-strain curves for the metallic glass heterostructures indicate that the spatial distribution of free volume ξ is significantly influenced by the configuration of the pores (Fig. 3). The shear zone confinement between the pores has effectively been established for sample I within shear zones of ~25 μm width (Fig. 3b). Fig. 3e demonstrates the stress-strain curves of the samples considered in Fig. 3b-d. In all of the three samples, the shear zone localization between the pores, which is initiated by the sharper stress drop, results in the structure to deform plastically until the fracture takes place.

Sample I with AB pore stacking and 50 μm lateral spacing between the pores shows the best performance with 3.83% fracture strain ε_f and 1.01 GPa ultimate compressive stress σ_{UCS}. A qualitative reasoning for this finding is that the amount of material compressibility changes with respect to the pore configuration. Helical material confinement exists between the neighboring pore stacks in the case of sample I and II, contributing to the overall plasticity, as well as to the linear elasticity of the sample (see Table 2).

Compared to the experimental results of the Zr-based monolithic metallic glass sample under compression where $\sigma_y = 1430$ MPa, $E = 86.9$ GPa [42], and calculated from the fully linear elastic response of a monolithic BMG until fracture $\varepsilon_y = 1.65\%$, the total fracture strain of sample I is 2.35 times higher at the expense of a ~30% drop in yield strength.

Figure 3 – Influence of pore configuration on the mechanical properties of the Zr-based bulk metallic glass as a function of free volume generation. Stress strain curves representing microstructures with varying pore configurations. (a) Schematic illustration of the constrained material between the pores for different pore configurations. (b) Enhanced mechanical properties are achieved when AB stacking configuration with 50 μm lateral pore spacing (sample I) is selected, which shows pronounced plastic deformation.(c) AB stacking pore

configuration with 50 μm vertical pore spacing (sample II) and (d) AA stacking pore configuration samples (sample III) with less than 3% total plasticity.

4.3 Influence of Porosity

Having determined the optimized pore configuration, porosity is another important parameter in the design of the optimal microstructure of a bulk metallic glass. Since type AB stacking configuration has been found to be the most effective pore configuration in terms of mechanical property enhancement, we now compare varying porosities at fixed AB stacking. Fig. 4 shows the distribution of free volume before fracture with respect to different porosities *P* (or pore diameters). The numerical results reveal that the 20% porous sample (sample I) exhibits the highest amount of deformation ($\varepsilon_f \sim 3.83\%$) through shear zone formation connecting the neighboring stacks (Fig. 4b). Sample IV with 10% porosity shows 2.42% fracture strain with relatively higher ultimate compressive strength of $\sigma_{UCS} = 1096$ MPa (Fig. 4a). A sharper decrease in the yield strength is observed during the shear band formation. On the other hand, sample V with 30% porosity (Fig. 4c) and sample VI with 45% porosity (Fig. 4d) exhibit a sudden failure before shear zones start to evolve between the pores. This phenomenon can be explained by the distribution of the stress fields depending on the porosity and pore configuration in the structure, where further discussion is provided in Section 5.5.

Table 2 summarizes the mechanical response of the samples with different pore configuration and porosity. Yield strain ε_y and yield strength σ_y values are measured from the first point where the deformation deviates from linearity [57]. The average Young's moduli E of the samples are consequently measured from the linear elastic part of the graphs.

Figure 4 – Effect of porosity on mechanical behavior of BMGs. (a) Sample IV with 10% porosity displays the highest yield strength ($\boldsymbol{\sigma_P = 1100}$ **MPa***) with* $\boldsymbol{\varepsilon_P = 2.4}$%. *(b) BMG heterostructure with 20% porosity (sample I) displays pronounced stress-strain response. (c-d) In contrast, change in porosity significantly alters the deformation behavior, which reduces the total deformation (*$\boldsymbol{\varepsilon_P}$ *~ 0.25% sample V and* $\boldsymbol{\varepsilon_P} \leq$ *0.10% for sample VI).*

Heterostructure	P (%)	E (GPa)	σ_y (MPa)	σ_{UCS} (MPa)	σ_f (MPa)	ε_y (%)	ε_f (%)
Sample I	20.0	51.0	824.0	1009.0	777.0	1.63	3.83
Sample II	20.0	58.3	829.0	833.28	668.3	1.43	2.71
Sample III	20.0	49.8	678.0	950.7	708.0	1.36	2.59
Sample IV	10.0	68.3	882.0	1096.0	807.4	1.30	2.42
Sample V	30.0	39.3	736.0	823.0	823.0	1.88	2.15
Sample VI	45.0	27.0	617.0	622.0	622.0	2.28	2.30

Table 2 – Summary of the numerically determined mechanical properties of metallic glass heterostructures with periodic pore distribution.

4.4 Stress-Strain Response of Shear Evolution

Fig. 5 compares the free volume distribution at different deformation states for sample I. Fully linear elastic behavior is observed at ~1.0 % deformation (Fig. 5a), where slight deviation from linear elasticity is observed when the deformation approaches 2% strain (Fig. 5b). After reaching its yield strength, uneven free volume distribution between rows of the AB pore stack start prevailing (Fig. 5c-d), which eventually results in shear band confinement at three major locations (Fig. 5e). Further deformation causes the free volume to accumulate particularly at the tip of the pores within the shear zones (e.g., see the middle right pore in Fig. 5f), leading to an instant stress drop and fracture.

Figure 5 – Deformation pattern of the sample I (20% porosity, AB stacking configuration), where the contour plots of the free volume distribution ξ are linked to the stress strain response.

4.5 Stress Distribution in Different Heterostructures

The contour plots shown in Fig. 6 exhibit the normal (σ_{22}) and shear stress (τ_{12}) components of the Cauchy stress tensor. For sample I, gradual distribution of the normal stress occurs in the horizontal direction between the pores perpendicular to loading. The bilateral stress fields connecting the pores encircle a wide region of almost two times larger diameter compared to the size of the pores (Fig. 6a). Thus, uniform stress distribution is induced before and after shear confinement between the pores takes place. Moreover, shear stress is evenly distributed between the neighboring stacks as well (Fig. 6b), enabling the shear to develop in a controlled and stable

manner at around 3.0% strain, where the stress drop at this strain represents the localized shear zone formations (Figs. 3e & 4e). The main difference of sample I from sample II and III is that the pore configuration in sample I controls the shear distribution more effectively, which results in homogeneous shear zone formation at different directions and angles. In contrast, when the shear zones initate in sample II and III, due to the lack of bilateral stress fields between the pores in the lateral direction perpendicular to loading, the developed shear zone tends to propagate in the diagonal direction determined by the pores where the resolved stress is at maximum (Fig. 6c-f).

For sample VI, the stress concentration is highly accumulated perpendicular to the loading direction (σ_{avg} ~1600 MPa) (Fig. 6g) between the pores, resulting in non-uniform stress distribution in the elastic regime. Compared to other samples, relatively higher average shear stress between different stacks (τ_{avg} ~500 MPa) with an angle larger than 90º causes early fracture with no observable plasticity (Fig. 6h). For this type of heterostructure, concentrated stress regions are observed in the near vicinity of the pores perpendicular to the applied stress, leading to early non-desired fracture.

Figure 6 – Influence of porosity on stress distribution. Stress concentrations around the pores due to the normal stresses in y-direction (σ_{22}) and shear component on xy-plane (τ_{12}) right before fracture for (a, b) sample I, (c, d) sample II, (e, f) sample III, and (g, h) sample VI.

4.6 Influence of Diameter-to-Spacing Ratio

In experiments of [17], it was shown that the ratio of pore diameter to lateral spacing between pores perpendicular to the loading direction (d/s) is another important factor which directly influences the mechanical response of the metallic glass heterostructures. Fig. 7a illustrates the numerically determined energy absorption values per unit volume W (area below the stress-strain curve) as a function of d/s ratio. The enhanced mechanical properties with 2.2% plasticity and ultimate compressive strength of 1010 MPa are observed if $d/s = 1$, which is the case for sample I with $d = s = 50\ \mu m$ ($P = 20\%$). Because of the extended plasticity values and high yield strength, the energy absorption of sample I reaches 28 MPa $s^{-1/2}$. Compared to the rough estimation of a typical compression response of a monolithic Zr-BMG

sample showing negligible plasticity [42], the total energy absorption for this bulk sample is estimated to be ~11.8 MPa, which is 2.35 times smaller than that of sample I. Similarly, W for sample II ($P = 20\%, d = 50\ \mu m, s = 83.3\ \mu m, d/s = 0.6$), sample III ($P = 20\%, d = s = 50\ \mu m, d/s = 1$), and sample IV ($P = 10\%, d = 35\ \mu m\ s = 65\ \mu m, d/s = 0.538$) are higher than their monolithic counterparts because of the shear-dominated deformation. With the normalization factor (by dividing the energy absorption by the ratio of the solid part of the heterostructure), the energy absorption for sample I exhibits ~3 times higher energy than its monolithic counterpart. As it can be also deduced from Table 2 and 3, sample I with 20% porosity and AB pore stacking configuration outperforms the other heterostructures of interest in terms of the overall plasticity and energy absorption per unit volume.

On the contrary, other samples having $d/s = 1.666$ (sample V: $P = 30\%, d = 62.5\ \mu m, s = 37.5\ \mu m$) and 3 (sample VI: $P = 45\%, d = 75\ \mu m, s = 25\ \mu m$) show lower energy absorption compared to samples with $d/s = 0.6$ and 1, which can be accounted for the suppression of the shear development as described in Figs. 5 and 6.

5. Comparison with Experimental Data

Energy absorption values for different porosities under tensile and compression mode are comparatively given with the experimental results in Fig. 7b. An analogous behavior to the numerical study of heterostructures with circular pores under compression is observed in the experimental study of the tensile heterostructures with circular pores under uniaxial tension (Fig. 1c & 2a), where the energy absorption is maximized at $P = 20\%$ (or d/s ratio). For higher porosities, the tensile data displays a drop in energy absorption because of the highly localized stress concentrations between the pores. A similar behavior has been observed for the simulations of the compression samples (Fig. 4c-e). Tensile samples under uniaxial deformation gain from the elastic stretching (comprising ~60-70% of the fracture strain) [17], which is reflected on the relatively higher energy absorption values than that of the numerical study of compression samples.

The experimental in-plane compression test of heterostructures with circle-like pores (as shown in Figs. 1b & 2b) show similarities compared to the other two datasets. Energy absorption of this structure maximizes around 25-30%, and retains high energy absorption

capacity at higher porosities (see the structure with 42% porosity). This behavior can be accounted for the extensive amount of in-plane elastic bending of the ligaments during compression depending on the porosity of the sample [19]. The correlated stress-strain response illustrates similarities for the compression heterostructures with circle-like pores and numerical simulations with circular pores in terms of ultimate compression strength and strain, where the elasticity of the ligaments in the high porosity ($\geq$ 42%) heterostructures with circle-like pores results in higher fracture strain values. On the other hand, heterostructures with circular-pores at lower porosities exhibit plastic strain because of the homogenous distribution of stress in the vicinity of a circle during in-plane compression pores (Fig. 8a-b). Significant fracture stress and strain for the tensile heterostructures is particularly obtained for the optimized porosity range of 20%, which shows multiple shear band formation between the lateral spacing of pores perpendicular to the loading direction (Fig. 8c) [17]. Table 3 summarizes the three datasets under investigation with respect to their energy absorption capacities per unit volume.

Figure 7 – (a) Energy absorption per unit volume as a function of diameter to spacing ratio (d/s). Ideal mechanical properties are attained with AB pore configuration and d/s ratio equal to 1. (b) Comparison of numerical and experimental studies of samples with AB pore configuration as a function of porosity. Error bars indicate the standard deviation of the mean values from at least three test samples. The results show similar behavior especially when the energy absorption per unit volume is maximized around 20% porosity. Note that the energy absorption has logarithmic scale to compare the deformation trends between different datasets.

Figure 8 – Comparison of stress –strain curves for the (a) experimental study of heterostructures with circle-like pores under in-plane compression, (b) experimental study of heterostructures with circular pores under uniaxial tension, and (c) numerical results for the compression of the heterostructures with circular pores.

Porosity vs. W (MJ/m^3)	10%	14%	20%	20%†	20%$^{¥}$	30%	35%	42%	45%	50%	60%
Compression Heterostructure (FEA)	17.3	-	27.7	15.0	16.3	9.0	-	-	7.2	-	-
Normalized with porosity (FEA)	19.2	-	34.6	18.8	20.4	12.9	-	-	13.1	-	-
Tensile Heterostructure (Exp.)	32.5	-	71.8	-	-	64.2	42.2	-	17.9	10.6	-
Compression Heterostructure (Exp.)	-	12.8	-	-	-	-	-	16.5	-	-	13.1

Table 3 – Comparison of experimental and numerical results including samples of different porosities as a function of energy absorption per unit volume W. † AB pore configuration with constant vertical spacing (50 µm) of pores, $^{¥}$ AA pore configuration. All the other samples have AB pore configuration with constant horizontal spacing (50 µm) of pores.

6. Discussion

The pursued numerical and experimental approach targets to solve the common drawbacks of the currently used strategies by quantitative structural property analysis. To this extent, second phase parameters such as pore size, spacing, configuration, as well as porosity are varied over a wide scale to assess the contribution of individual variations on the mechanical response. The gradient-extended thermodynamically consistent material model is implemented for metallic glass heterostructures, where localized shear zone formation is observed at the plastic regime for the heterostructures with ≤ 20% porosity and different pore configurations under constant rate of quasi-static loading conditions. Among these, sample I with 20% porosity and AB pore stacking with constant lateral pore spacing of 50 µm shows the most advanced properties in terms of elastic and plastic response and energy absorption capacity. Furthermore, all six numerical samples outperform experimentally measured energy absorption capacity of the monolithic metallic glass normalized by their own porosities.

The results highlight the importance of determining the right values for each individual parameter as well as the interplay of experimental and computational investigations. The findings prove that in contrast to the reported hypothesis, not only the spacing, but also the size and configuration of the pores, and the amount of porosity are as much effective in controlling the shear propagation.

It is found that the porosity has a higher influence on the overall mechanical response compared to the effect of the pore configuration. The numerically calculated final fracture strain of the optimized sample is found to have 2.35 times higher compared to the experimentally

determined monolithic metallic glass sample at the expense of only a slight decrease in yield strength. This improvement is expressed as the overall toughness of the considered sample, which has around three times higher energy absorption per unit volume normalized by its porosity. The experimental results suggest a very similar deformation, where the tensile heterostructure with $P = 20\%$ ($d/s = 1$) ratio and AB stacking configuration shows an optimum fracture strain at the negligible expense of fracture strength, resulting in relatively higher energy absorption compared to other porosity values.

7. Conclusion

Overall, the study presented in this paper addresses the key factors to understand the deformation mechanisms in bulk metallic glass heterostructures. Due to the flexibility of the design in both numerical and experimental methods, this novel approach can also be utilized to predict the behavior of other periodic or randomized pore designs with different shapes and sizes in the same structure. The findings proved that in contrast to the reported hypothesis, not only the spacing, but also the size and configuration of the pores, and the amount of porosity are as much effective in controlling the shear propagation.

This semi-empirical numerical approach allowed examining the deformation mechanics of metallic glass heterostructures. The numerical analysis provided an original way to make accurate predictions of the deformation behavior of the actual samples, which are generally challenged by the out-of-plane buckling during in-plane compression experiments. Moreover, the scalability of the pursued numerical method allowed predicting the behavior of different types of porous metallic glasses on multiple-length scales. The repeatable microstructure pattern used in this numerical study, which consists of a representative volume element with applied periodic boundary conditions, can further provide a guideline for real applications on a macro-scale level.

Acknowledgements

The authors would like to thank Edgar Husser, Dr. Ingo Scheider and Dr. Dirk Steglich for the fruitful discussions. The authors would also want to thank Prof. Jan Schroers for the experimental studies conducted at Yale University under his supervision.

8. References

[1] Schroers J, HollandMoritz D, Herlach DM, Grushko B, Urban K. Mat Sci Eng a-Struct 1997;226:990.
[2] Schwarz M, Karma A, Eckler K, Herlach DM. Phys Rev Lett 1994;73:2940.
[3] Ashby MF, Greer AL. Scr Mater 2006;54:321.
[4] Greer AL. Mater Today 2009;12:14.
[5] Schroers J. Adv Mater 2010;22:1566.
[6] Johnson WL. Mrs Bull 1999;24:42.
[7] Schroers J. Phys Today 2013;66:32.
[8] Schroers J. Jom-Us 2005;57:35.
[9] Kumar G, Tang HX, Schroers J. Nature 2009;457:868.
[10] Guo H, Yan PF, Wang YB, Tan J, Zhang ZF, Sui ML, Ma E. Nat Mater 2007;6:735.
[11] Volkert CA, Donohue A, Spaepen F. J Appl Phys 2008;103.
[12] Schuh CA, Lund AC, Nieh TG. Acta Mater 2004;52:5879.
[13] Ma H, Xu J, Ma E. Applied Physics Letters 2003;83:2793.
[14] Launey ME, Busch R, Kruzic JJ. Acta Mater 2008;56:500.
[15] He G, Eckert J, Loser W, Schultz L. Nat Mater 2003;2:33.
[16] He G, Eckert J, Loser W, Hagiwara M. Acta Mater 2004;52:3035.
[17] Sarac B, Schroers J. Nat Commun 2013;4.
[18] Sarac B, Ketkaew J, Popnoe DO, Schroers J. Adv Funct Mater 2012;22:3161.
[19] Sarac B, Schroers J. Scr Mater 2013;68:921.
[20] Falk ML, Langer JS, Pechenik L. Phys Rev E 2004;70.
[21] Falk ML, Shi YF. Mater Res Soc Symp P 2003;754:257.
[22] Li QK, Li M. Mater Trans 2007;48:1816.
[23] Liu HB, Li JF, Cao QP, Zhou YH. Chinese Sci Bull 2007;52:3443.
[24] Yamakov V, Wolf D, Salazar M, Phillpot SR, Gleiter H. Acta Mater 2001;49:2713.
[25] Yamakov V, Wolf D, Phillpot SR, Gleiter H. Acta Mater 2002;50:61.
[26] Lund AC, Schuh CA. Acta Mater 2005;53:3193.
[27] Torquato S, Stillinger FH. Rev Mod Phys 2010;82:2633.
[28] Song C, Wang P, Makse HA. Nature 2008;453:629.
[29] Bernal JD, Mason J. Nature 1960;188:910.
[30] Bernal JD. Nature 1960;185:68.
[31] Pusey PN, Vanmegen W. Nature 1986;320:340.
[32] Vanblaaderen A, Wiltzius P. Science 1995;270:1177.
[33] Royall CP, Poon WCK, Weeks ER. Soft Matter 2013;9:17.
[34] Schall P, Weitz DA, Spaepen F. Science 2007;318:1895.
[35] Huang R, Suo Z, Prevost JH, Nix WD. J Mech Phys Solids 2002;50:1011.
[36] Gao YF. Model Simul Mater Sc 2006;14:1329.
[37] Zheng GP, Li M. Phys Rev B 2009;80.
[38] Thamburaja P. J Mech Phys Solids 2011;59:1552.
[39] Steif PS, Spaepen F, Hutchinson JW. Acta Metall Mater 1982;30:447.
[40] Bargmann S, Xiao T, Klusemann B. Philos Mag 2014;94:1.
[41] Klusemann B, Bargmann S. J Mech Behav Mater 2013;22:51.
[42] Duan G, Wiest A, Lind ML, Li J, Rhim WK, Johnson WL. Adv Mater 2007;19:4272.

[43] Kumar G, Desai A, Schroers J. Adv Mater 2011;23:461.
[44] Sarac B, Kumar G, Hodges T, Ding SY, Desai A, Schroers J. J Microelectromech S 2011;20:28.
[45] Sarac B. Artificial microstructures to investigate microstructure-property relationships in metallic glasses. vol. Doctoral Dissertation. Ann Arbor: ProQuest/UMI,: Yale University, 2013.
[46] Gurtin ME, Needleman A. J Mech Phys Solids 2005;53:1.
[47] Thamburaja P, Ekambaram R. J Mech Phys Solids 2007;55:1236.
[48] Heggen M, Spaepen F, Feuerbacher M. Mat Sci Eng a-Struct 2004;375:1186.
[49] Demetriou MD, Johnson WL. J Appl Phys 2004;95:2857.
[50] Spaepen F. Acta Metall Mater 1977;25:407.
[51] Vandenbeukel A. Scripta Metall Mater 1988;22:877.
[52] Zheng GP, Shen Y. Int J Solids Struct 2010;47:320.
[53] Ekambaram R, Thamburaja P, Yang H, Li Y, Nikabdullah N. Int J Solids Struct 2010;47:678.
[54] Lewandowski JJ, Wang WH, Greer AL. Phil Mag Lett 2005;85:77.
[55] Faupel F, Frank W, Macht MP, Mehrer H, V N, Ratzke K, Schober HR, Sharma SK, Teichler H. Rev Mod Phys 2003;75:237.
[56] Bargmann S, Ekh M, Runesson K, Svendsen B. Philos Mag 2010;90:1263.
[57] Demetriou MD, Launey ME, Garrett G, Schramm JP, Hofmann DC, Johnson WL, Ritchie RO. Nat Mater 2011;10:123.