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Structural origins for the generation of strength, ductility and toughness in bulk-metallic glasses using hydrogen microalloying



L.S. Luo ^a, B.B. Wang ^{a, **}, F.Y. Dong ^b, Y.Q. Su ^{a, ***}, E.Y. Guo ^c, Y.J. Xu ^d, M.Y. Wang ^d, L. Wang ^a, J.X. Yu ^e, R.O. Ritchie ^{f, g, *}, J.J. Guo ^a, H.Z. Fu ^a

^a National Key Laboratory for Precision Hot Processing of Metals, School of Materials Science & Engineering, Harbin Institute of Technology, Harbin, 150001, China

^b School of Materials Science & Engineering, Shenyang University of Technology, Shenyang, 110870, China

^c School of Materials Science & Engineering, Dalian University of Technology, Dalian, 116024, China

^d AVIC Manufacturing Technology Institute, Beijing, 100024, China

^e Center of Analysis & Measurement, Harbin Institute of Technology, Harbin, 150001, China

^f Department of Materials Science & Engineering, University of California, Berkeley, CA, 94720, USA

^g Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA

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ABSTRACT

A vital requirement for bulk-metallic glasses (BMGs) as structural materials is the attainment of both strength and toughness, yet invariably, as in most materials, these properties are mutually exclusive. However, by utilizing a hydrogen microalloying technology, involving alloying with a gas mixture of hydrogen/argon, we have converted "strong-yet-brittle" bulk-metallic glasses into "stronger-and-tough" ones. We combine experiments with molecular dynamics simulations to systematically analyze the atomic-scale details on how trace hydrogen additions can induce internal changes in the amorphous structure of Zr-Cu-based glassy alloys, with the aim of discerning the structural origin of the combined high strength, ductility and toughness of these materials. Our results, from both relaxation spectrum analysis and calculations of the atomic configurations, indicate that minor additions of hydrogen, instead of causing embrittlement, can have a positive influence on the mechanical properties of BMGs. Specifically, they generate more highly activated "soft spots" to promote multiple shear bands to enhance deformability, yet at the same time engender the formation of a more strengthened structural matrix to delay their initiation, a factor which can serve to elevate strength. Accordingly, our H-alloyed samples display a larger yield strength and fracture strain than the H-free ones. The current findings not only show how the strength-toughness trade-off can be successfully overcome in bulk-metallic glasses, but also we regard this understanding as a step forward to decoding the salient underlying mechanisms for the correlating structure, relaxation behavior and mechanical properties of these materials.

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1. Introduction

As a new class of potential structural materials, bulk-metallic glasses (BMGs) are of great interest to the materials science community due to their unique mechanical properties, in particular their generally high strength with comparatively large elastic strains [1–4]. Nevertheless, the often poor deformability of BMGs at ambient temperatures represents an "Achilles' heel" which has severely compromised their potential application as engineering structural materials [5–7]. For monolithic BMGs, the plastic deformation behavior is primarily affected by their alloy chemical composition [8,9], and/or externally driven processes [10–13] which can be ascribed to changes in the corresponding structure in the amorphous state. For instance, thermal cycling of BMGs can "rejuvenate" their amorphous structures to improve plasticity but often at the sacrifice of strength [10]. Alternatively, minor additions of specific elements or microalloying techniques, which have been

^{*} Corresponding author. Department of Materials Science & Engineering, University of California, Berkeley, CA, 94720, USA.

^{**} Corresponding author.

^{***} Corresponding author.

E-mail addresses: 14B909043@hit.edu.cn (B.B. Wang), suyq@hit.edu.cn (Y.Q. Su), roritchie@lbl.gov (R.O. Ritchie).

traditionally used in conventional polycrystalline alloys, also appear to be an effective method for generating BMGs with improved ductility, strength and toughness [8,14].

In this regard, it has been found that surprisingly the addition of hydrogen atoms can significantly enhance the mechanical behavior of several glassy alloys using such methods of gas-permeation or cathodic charging [15–19]. However, both these hydrogenation processes are complex and costly: furthermore, sample sizes that can be treated are mostly restricted to the micrometer scale [20,21]. In contrast to such traditional hydrogenation methods, we have recently explored a new method of incorporating tiny amounts of hydrogen atoms directly into Zr-Cu-based BMGs by melting master alloys under the gaseous mixture of H₂/Ar, a process that we term "melt hydrogenation" [22–25]. Strikingly, minor doping amounts of hydrogen, e.g., 210 wppm, can simultaneously improve the compressive strength (or glass-forming ability), ductility and toughness of BMGs [22-24]. Moreover, there are several other advantages of this microalloying technology in that: (i) it is a simple and inexpensive method that is far more suitable for large-sized BMGs components than the other two hydrogenation methods, (ii) it does not simply apply to a specific alloy but is applicable to wide range of glass-forming alloys with hydrogen-affine base elements, (iii) it can be used to remove oxygen impurities during the smelting stage [25], and (iv) the hydrogenated Zr-based BMGs retain a constant hydrogen concentration over time, with a positive long-term effect on deformability [26]. This hydrogen microalloying method has received increasing attention and further efforts are being made to develop this technique as a major processing route for BMG allovs [26–28]. Unfortunately, the micromechanisms underlying the improvements in the toughness of BMGs (without sacrificing strength) from hydrogenation are still unknown, a situation that results from our limited understanding of hydrogen-induced structural changes in the amorphous state [29.30].

Accordingly, it is the purpose of the current work to develop a theoretical framework -for this microalloying procedure in an attempt to gain further insight into the structural metrics of the alloy-dependent deformation behavior observed in BMGs. Microscopically, the deformation of glassy alloys is proposed to be accommodated by the cooperative shear motion of local events involving several tens or hundreds of atoms, termed sheartransformation zones (STZs) [31-33]. The detected "soft spots", i.e., relatively loosely packed regions, are deemed to be more likely to initiate such local rearrangements [34–36]. Either applied stress or elevated temperatures, which can induce global plasticity or relaxations in amorphous alloys, are considered to activate and percolate these flow units [37,38]; consequently, we can conclude that the relaxation dynamics are inherently connected to the underlying deformation mechanisms that govern the strength and deformability of amorphous alloys [39–41]. The primary (α) relaxation takes place through activated events involving compact regions (irreversible process), and is responsible for the glass transition and yielding [40-44]. Correspondingly, the secondary or Johari-Goldstein (β) relaxation, which is governed by percolationlike clusters of particles like STZ (reversible process), is fundamental to our considerations of the mechanical properties of glassy alloys [45–48]. Based on an extensive study of a variety of metallic glasses (MGs) over a wide range of temperatures, Wang et al. recently identified a further secondary relaxation processes, specifically, the existence of a low-temperature fast (β') relaxation beyond the β -relaxation [49,50]. These authors demonstrated that this fast relaxation is strongly correlated with the topological heterogeneity and the reversible anelastic motion of atoms physically confined by the elastic matrix; as such, it presents another triggering process for plasticity in glassy alloys [49].

Accordingly, by systematic scrutiny of the dynamic relaxation spectroscopy in H-free and H-alloyed Zr-Cu-based BMGs, we demonstrate a strong hydrogenated effect on the behavior of the β' relaxation. Specifically, compared to the H-free alloys, there are more dissipative units (*i.e.*, "soft spots") in the H-alloyed alloys which contain more easily activated atoms during deformation. At the same time, the elevated activation energy for β -relaxation and α -relaxation (a characteristic of stronger matrixes), due to the minor additions of hydrogen, endows these alloys with higher strength. To analyze these amorphous atomic-scale details, in this work we apply molecular dynamics (MD) simulations with a scenario for structural analysis based on our local "gradient atomic packing structure" model [51], which gives a definite structure for the so-called "soft spots".

2. Methods

2.1. Sample preparation

In this work, two BMG materials were studied: (i) $Zr_{64}Cu_{24}Al_{12}$ (at.%) rods, with diameter 3 mm and lengths up to 50 mm, and (ii) $Zr_{55}Cu_{30}Al_{10}Ni_5$ (at.%) plates, with the dimensions of $50 \times 10 \times 1$ and $60 \times 30 \times 2$ mm³, respectively. All ingots were prepared by arcmelting mixtures of pure elements (with the purity of above 99.9 at.%), and remelted at least four times to obtain chemical homogeneity. Eventually, suction-casting of these master alloys was performed using the water-cooled copper moulds with different dimensions. During these procedures, a pure argon atmosphere was employed to obtain H-free samples, whereas the H-alloyed samples were alloyed under an of 85% argon mixed with 15% hydrogen.

2.2. Experimental characterization

X-ray diffraction (XRD) was carried out (with Bragg-Brentano geometry and Cu K α radiation) to verify that the samples remained fully glassy throughout. Hydrogen concentrations were measured using an oxygen-hydrogen analyzer (LECO ROH600, Saint Joseph, MI, USA); the hydrogen released from the samples was oxidized to water to enable detection using non-dispersive infra-red cells. Ultrasonic methods, using an Olympus Panametrics (NDT 5900 PR, Waltham, MA, USA), were employed to obtain the elastic properties of the BMGs from the acoustic velocities and density measurements [1]; the latter was achieved using the Archimedes method to an accuracy of ~1.0%. The interaction of hydrogen with specific elements was further analyzed using x-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, ThermoFisher, USA) with monochromatized Al K_{α} excitation. The specimens were thoroughly cleaned prior to being placed in the spectrometer where they were sputtered using Ar ion bombardment to ~1 µm thickness to remove any oxide or other contaminants.

Instrumented nanoindentation was performed using a Nanoindenter-G200 (Agilent, Santa Clara, CA, USA) at room temperature under load control up to a maximum load of 100 mN. A cube-corner diamond indenter that is sharper than the common Berkovich indenter was used to produce significantly higher level of stress and strain beneath the contact; its area function was calibrated using fused silica standards. Samples were loaded to a maximum load of 100 mN, then maintained at that load for 10 s before unloading; loading and unloading rates were 1 mN s⁻¹, with the drift rate maintained below 0.05 m s⁻¹. After fracture toughness and nanoindentation tests, fracture surfaces and indenter impressions were imaged with a scanning electron microscopy (SEM), using a JXA-8230 electron probe microanalyzer (JEOL,

Akishima, Japan) operating under the secondary-electron imaging mode.

The relaxation behavior of the BMGs was characterized using a dynamical mechanical analyzer (DMA, TA Q800, Texas Instruments, New Castle, DE, USA). The dynamic modulus $E(\omega) = E'(\omega) + iE''(\omega)$, where the real part E' and imaginary part E'' respectively represent the storage and loss modulus, was measured in single cantileverbending with a single frequency of 1 Hz for $Zr_{64}Cu_{24}Al_{12}$ and a discrete frequency of 0.5 Hz, 1 Hz, 2 Hz, 4 Hz for $Zr_{55}Cu_{30}Al_{10}Ni_5$. For these isochronal DMA tests, each rectangular specimen, with dimensions of $30 \times 2 \times 1 \text{ mm}^3$, was first cooled to 165 K and then retained at this temperature for 1 min before ramping up the temperature at a constant heating rate of 2 K min⁻¹.

2.3. Atomistic simulations

Based on the second nearest-neighbor modified embeddedatom method (2NN MEAM) [52], the recently developed Cu-Zr-H ternary potential, whose reliability has been confirmed [53], was employed to carry out the MD calculations using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [54]. A prototypical Zr₅₀Cu₅₀ (at.%) system was selected to study the hydrogenation behavior of the ZrCu-based amorphous alloys. The amount of inserted hydrogen atoms was denoted by the N_H/N_M ratio, defined as the ratio of the number of inserted hydrogen atoms (N_H) to that of the Cu and Zr atoms (N_M) . During the MD simulations, five independent groups of H-free $(N_H/N_M = 0 \text{ at.}\%)$ and Halloyed $(N_H/N_M = 2 \text{ at.}\%)$, similar to the content of experimental specimens) samples were prepared with different dimensions and cooling rates (S1: N_M = 10,000, 0.01 K/ps, S2: N_M = 10,000, 0.1 K/ps, S3: $N_M = 150,000, 0.1 \text{ K/ps}, \text{ S4: } N_M = 320,000, 0.1 \text{ K/ps}, \text{ and } \text{S5:}$ $N_M = 10,000, 1 \text{ K/ps}$). Each sample with periodic boundary conditions (PBCs) was first held at 2000 K for 2 ns (time step 1 fs), and then cooled to the glassy state (at 300 K) under an isothermalisobaric ensemble (NPT). The temperature was controlled by the Nose-Hoover thermostat [55], and the external pressure was held at zero by using a Parinello-Rahman barostat [56].

For the mechanical simulations, three loading schemes were employed. First, uniaxial compression deformation with a constant strain rate of 10^8 s^{-1} along the z-axis was applied on group S4, all with dimensions of 22.7 (x) \times 5.6 (y) \times 44.8 (z) nm³, at ambient temperature (300 K). Second, to directly compare the degree of deformability, group S3, with similar dimensions of 16.8 (x) \times 2.9 (y) \times 54.5 (z) nm³, was subjected at 300 K to uniaxial tensile loading along the x-axis at a strain rate of 10⁸ s⁻¹. During these two processes, consistently PBCs were imposed in the y- and z-directions with a free surface in the xdirection to allow for the occurrence of a shear offset at the free surfaces; a Parrinello-Rahman barostat was employed in the y-direction, perpendicular to the loading direction, to achieve a stress-free state. To relax the surfaces, all samples were annealed at 300 K for 1 ns. Third, pure shear loading (supercell tilting) was imposed on the group S1, with the similar dimension of $5.5 \times 5.5 \times 5.5$ nm³, at 300K at a shear strain rate of 10⁶ s⁻¹. PBCs were applied for all three dimensions to eliminate any surface effects.

The local atomic structures of the glassy systems were identified by using the weighted Voronoi tessellation method [57,58]. As our samples comprise more than one species which have significant size differences, the perpendicular bisectors between the central atom and corresponding neighboring atoms were weighted by the atomic size to make up a Voronoi polyhedron. This polyhedron is usually indexed as < n_3 , n_4 , n_5 , n_6 > to describe the topology and arrangement of the nearest-neighbor atoms around the central atom; specifically, n_i represents the number of *i*-edged polygons. The post visualization and analysis of the atomic strain was realized in the program OVITO [59].

Fig. 1. X-ray diffraction traces for Zr-Cu-based BMGs with different hydrogen contents. (a) For rods of $Zr_{64}Cu_{24}Al_{12}$; (b) for plates of $Zr_{55}Cu_{30}Al_{10}Ni_5$. All samples remain fully vitrified.

3. Results

3.1. Multi-scale mechanical behavior

The average hydrogen concentrations, determined by inert-gas analysis, were measured at 264 and 247 wt.ppm (~2 at.%), respectively, for the H-alloyed $Zr_{64}Cu_{24}Al_{12}$ and $Zr_{55}Cu_{30}Ni_5Al_{10}$ glasses. Both materials were fully amorphous, as shown by the XRD spectra for both BMGs, in the H-free and H-alloyed conditions, which feature patterns characteristic of the glassy state (Fig. 1).

According to previous uniaxial compression tests by ourselves [24] and others [17,26], incorporating small amounts of hydrogen atoms into Zr-Cu-based BMGs can promote an increase in their yield strength, yield strain, ultimate strength and fracture strain, as listed in Fig. 2a.¹ In this work, to illustrate that the H-induced toughness was not simply due to experimental scatter in the compression tests [61], we conducted fracture toughness measurements in the three-point bending configutation using precracked beams. As seen in Fig. 2b, the load-displacement data are found to show a slight visible deviation from linearity just prior to failure such that the peak load at breaking point can be employed as a valid measurement of the plane-strain fracture toughness. Based on ASTM Standard E399 for fracture toughness measurement, the calculated critical stress intensity K_{IQ} at fracture varied from 84 MPa m^{1/2} to 101 MPa m^{1/2} due to the progressive incorporation of small amounts of hydrogen. We further examined the morphology of these fractures corresponding to different hydrogen contents, as shown in Fig. 2c-f. The mechanistic origin of fracture toughness in MGs could be understood as crack blunting due to multiple shear banding and/or potential crack arrest accommodated by sliding along shear bands ahead of the crack tip [5]. In essence, as BMGs invariably display high strength, the creation of such multiple shear banding, which promotes plasticity, is synonymous with the concomitant development of fracture toughness. In the fractographs of Fig. 2c and d, the "rough zone width" W_R , which



¹ The yield points (corresponding to the initiation of shear-bands) are determined by the crossover point from the elastic to plastic deformation with a strain offset of 0.05% [60].



Fig. 2. Improved mechanical properties of BMGs after hydrogen microalloying. (**a**) Results from room temperature compression tests, showing the yield strength σ_{yy} , yield strain ε_{y} , ultimate strength σ_{m} , and fracture strain ε_{f} , for rods of Zr₃₅Cu₆₅ (Zr35), Zr₅₀Cu₅₀ (Zr50), Zr₆₄Cu₂₄Al₁₂ (Zr64), Zr₅₅Cu₃₀Al₁₀Ni₅ (Zr55), and Zr₅₇Cu_{15,4}Al₁₀Ni_{12,6}Nb₅ (Zr57) BMGs [17,24,26]. (**b**) Typical load-displacement diagram for the SENB specimens of Zr₅₅Cu₃₀Al₁₀Ni₅. The inset presents the geometry of a SENB configuration. Scanning electron micrographs of the fracture surfaces from (**c**,**e**) the H-free, and (**d**,**f**) the H-alloyed fractured specimens. Subfigures (**e**) and (**f**) are respectively details of (**c**) and (**d**) indicated by the yellow squares. The "rough zone width" W_R in (**c**) and (**d**) is also marked by dash lines. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

is approximated graphically by determining the level where steep ridges and deep valleys merge, designates the extent of shear sliding activity ahead of the pre-crack [62]. As seen, the W_R also increases with minor additions of hydrogen. In addition, comparing Fig. 2e with Fig. 2f, the fracture surface of the tough H-alloyed sample consists of a more developed and dense vein-like pattern. Similarly, the addition of H was found to increase the fracture load (from 2500 to 2750 N) and deflection (from 0 to 5 mm) in bending tests on unnotched $Zr_{55}Cu_{30}Al_{10}Ni_5$ plates [22]. Using the analysis of Conner et al. [63], one can semi-quantitatively evaluate an approximate critical mode I stress intensity K_{Ic} , from a knowledge of the bending strain at fracture; as such, we were able to conclude that the hydrogenated BMGs possess considerably higher fracture toughness than the H-free alloys.

. Moreover, a common observation from these tests was that during deformation, the population density of visible shear bands (SBs) present on the surface was always higher in the H-alloys BMGs than in the H-free specimens [22,24].

Based on instrumented nanoindentation measurements of the micro-scale mechanical behavior of the BMGs with different hydrogen contents, force-depth curves are displayed in Fig. 3a. Each arrow marks a first "pop-in" (initial yielding point), *i.e.*, a sudden increase in indenter displacement corresponding to the onset of SBs. In common with the macroscopic mechanics tests, the microscale H-alloyed specimen also presents a lagging yielding point, *i.e.*, an increased yield load and displacement. Scanning electron microscopy images of the intents, in Fig. 3b and c, indicate that more profuse SBs can be seen to form around the indenter in H-alloyed BMGs than in H-free alloys. Note that well below the glass-

transition temperature T_g , the deformability of amorphous alloys can be severely impeded by premature failure on one, or a few, dominant SBs; conversely, the ductility and toughness are improved by proliferation of SBs as the resulting plastic flow is more uniform [64]. Additionally, from ultrasound measurements (Table 1), the effect of hydrogen microalloying on the elastic constants of these BMGs is also small, especially compared to the marked effect on the toughness of these alloys; this may suggest that the deformation behavior is largely attributable to anelastic, *i.e.*, time-dependent elastic strains. Accordingly, we describe below our detailed analysis to look for clues as to why minor additions of hydrogen not only strengthen the BMGs, but facilitate the multiplication of SBs and hence their ductility and toughness.

3.2. Dynamic relaxation behavior

The relaxation spectra were characterized employing dynamic mechanical tests over a wide range of temperatures, from ~150 K to 750 K. Fig. 4a presents the temperature dependence of the loss modulus E''(T) measured at 1 Hz for $Zr_{64}Cu_{24}Al_{12}$ with different hydrogen contents. Akin to previous results [49], these spectra from the strong Zr-Cu-based MGs also show α - (or main) relaxation peaks around T_g [26], β - (or slow) relaxation excess wings (an excess contribution to the tail of the α -relaxation), and rather a smaller amplitude of β' - (or fast) relaxation peaks at lower temperature. After hydrogen microalloying, the superposition peak for α -relaxation and β -relaxation moves to a higher temperature with a relatively lower intensity; by contrast, a much higher intensity peak ($I_{\beta'}$) for β' -relaxation emerges at lower temperature. An atlas of



Fig. 3. Nanoindentation for rods of Zr₆₄Cu₂₄Al₁₂ BMGs. (a) Load-displacement curves of H-free and H-alloyed samples tested up to a maximum load of 100 mN. The initial yield load (first "pop-in") is indicated by the arrows. The indenter impressions of (b) the H-free, and (c) the H-alloyed specimens.

Table 1

Characteristic properties of H-free and H-alloyed Zr₅₅Cu₃₀Ni₅Al₁₀ BMGs^a.

H-free 687 6.871 32.0 109.8 0.367 49 152 444 ~15-41 H-alloyed 694 6.881 32.3 113.1 0.370 40 163 498 ~12-33	Status	$T_g/K(\pm 1)$	$ ho / { m g~cm^{-3}}~(\pm 0.01)$	G/GPa (±0.2)	<i>B</i> /GPa (±0.4)	$\nu(\pm 0.0005)$	$E_{\beta'}/\mathrm{kJ}~\mathrm{mol}^{-1}$	$E_{\beta}/\mathrm{kJ}~\mathrm{mol}^{-1}$	$E_{\alpha}/\text{kJ} \text{ mol}^{-1}$	$n (\gamma_c \sim 0.1 - 0.15)$
	H-free	687	6.871	32.0	109.8	0.367	49	152	444	~15-41
	H-alloyed	694	6.881	32.3	113.1	0.370	40	163	498	~12-33

^a Glass-transition temperature T_g [23], density ρ , shear modulus G, bulk modulus B, Poisson's ratio ν , activation energy E_{β} for the β' relaxation, E_{β} for the β relaxation, and E_{α} for the α relaxation, the estimated average number of anelasitc atoms n for the nucleation of STZs.

dynamic relaxation spectra for H-free and H-alloyed $Zr_{55}Cu_{30}Al_{10}Ni_5$ specimens with different frequencies is mapped in Fig. 4b; similarly, the evolution law of these E''(T) curves after incorporating small amounts of hydrogen follow an identical trend as the results in Fig. 4a.

In addition, as the driving frequency f is increased, each E''(T)curve in Fig. 4b shifts to a higher temperature. As plotted in Fig. 4c–e, the *f*-dependence of the characteristic temperature T_i for the various relaxations follows an Arrhenius relation, $f = f_0 \exp(-\frac{1}{2})$ E_i/RT_i), where f_0 is prefactor for the frequency of vibration depending on activation entropy, R is the gas constant, and E_i is the activation energy for different relaxations. Thus, the values of E_{α} for α -relaxation, E_{β} for β -relaxation, and $E_{\beta'}$ for β' -relaxation can be obtained from the plot of $\ln(f)$ versus $1/T_i$, as respectively listed in Table 1. (Note that the value of E_{β} for β -relaxation in strong glassy alloys with an excess wing was determined following the method described in Ref. [47]). From these data, it is clear that both the α and β -relaxation in H-alloyed samples require a higher energy to activate, which corresponds to a higher activation temperature; conversely, incorporating hydrogen atoms facilitates the β' -relaxation to be more easily activated.

The α -relaxation initiates at high temperature (T_g), which is responsible for vitrification, and thus controls the strength of the MGs [41,42]; a higher E_{α} means the collapse of "backbones" (*i.e.*, a high-modulus network) requires more external energy, *i.e.*, a larger yield stress and yield strain, for the onset of plastic deformation. The β -relaxation continues below the glass-transition temperature, and acts as a precursor to the glass transition [65], determining the feature of α -relaxation. The E_{β} follows an approximately linear relationship of $E_{\beta} \approx 24(\pm 2)RT_g$ [47], which conforms to the " β relaxation to α -relaxation" self-similar organization of the potential-energy landscape [40]. It is known that the flow phenomenon in MGs is the percolation of the localized motion units, such as STZs [37,66]. According to the cooperative shearing model [33], the E_{β} is equivalent to the potential-energy barrier for the percolation ("cage-breaking") of STZs [47], a higher value of E_{β} corresponding to a stronger matrix confinement. Moreover, the β relaxation, which is regarded as a thermal-driven percolation process of STZ events, correlates with intrinsic plasticity in glassy alloys [45,46]. Due to the complicated deformation mechanisms in MGs, consideration of only the β -relaxation, in particular the nonmonotonic relationship between Poisson's ratio ν and the energy barrier (or average volume) for the percolation of STZs [47,67], is not sufficient.

Compared to the β -relaxation, the unusual β' -relaxation is physically more localized at unstable regions ("soft spots"), which involve the most mobile or anelastic atoms. Indeed, the energy barrier for anelastic deformation in La-based MGs, measured using nanoindentation, is almost identical to their $E_{\beta'}$ [50]. Therefore, we can regard this fast relaxation as the nucleation or initiation of STZs, which is rooted in the topological heterogeneity of amorphous alloys. Additionally, as the values of $E_{\beta'}$ appear to be generally



Fig. 4. Dynamic mechanical analysis. Comparison of the values of the temperature-dependent loss modulus E''(T) of H-free and H-alloyed BMGs. (**a**) For $Zr_{54}Cu_{24}Al_{12}$ at a single frequency of 1 Hz, (**b**) for $Zr_{55}Cu_{30}Al_{10}N_{15}$ with discrete frequency, ranging from 0.5 to 4 Hz. The heating rate was 2K min⁻¹. The frequency-dependent (**c**) peak temperature of the α -relaxation, (**d**) selected temperature of the β -relaxation excess wing, and (**e**) peak temperature of the β' -relaxation in H-free and H-alloyed $Zr_{55}Cu_{30}Al_{10}N_{15}$ samples. The solid curves represent linear fits for the points from which the values of E_{α} , E_{β} , and $E_{\beta'}$ can be obtained using the Arrhenius relationship. The activation energy for β -relaxation is a mean of the slope of three fitted lines in (**d**).

insensitive to the glass-transition temperature [49], the precise nature of the β' -relaxation may provide an understanding of the origin of the plasticity in MGs, as distinct from their strength. Based upon the work of Fan et al. [68], the effective activation volume V_{eff} for the nucleation of STZs can be estimated from the equation, $E_{B'}$ $G = 1/2V_{eff}\gamma_c^2$, where G is the shear modulus and γ_c (~0.1–0.15) is the average strain caused by the local anelastic process [69]. Furthermore, this activation volume can be expressed as V_{eff} = $nC_f V_a$, where *n* is the number of activation atoms, $C_f (\approx 1.1)$ is a free volume parameter [70], and V_a is the atomic volume, which can be defined as $V_a = M/(\rho N_0)$; here ρ is the density, *M* is the molar mass and N_0 is the Avogadro constant. As a consequence, one can estimate the average number of anelastic atoms for the nucleation of STZs in the Zr₅₅Cu₃₀Al₁₀Ni₅ BMG with different hydrogen contents as: $n = V_{eff} \rho N_0 / (C_f M)$; these are listed in Table 1. Note that the total fraction of anelastic atoms in MGs should depend linearly on the intensity $I_{\beta'}$ of the β' -relaxation peak. More importantly, it has now been documented that STZs are likely to be nucleated at the "soft spots" that exist in MGs [34,36,71]. Thus, we would expect that the number of "soft spots" in a glassy sample to be directly proportional to the value of $I_{\beta'}/n$. The larger this ratio, the more "soft spots" are likely to be involved in instigating the deformation process; this in turn will result in an enhanced deformability in amorphous alloys, a notion which is examined for different glassy systems [49,72] in Fig. 5. In brief, H-alloyed BMGs, with their lower value of $E_{\beta'}$ and higher $I_{\beta'}/n$ ratio, possess a larger fraction of readily activated "soft spots" for the nucleation of STZs, thereby inducing multiple shear banding to promote plastic deformation, and ultimately toughness.

3.3. Electronic structure

The role of trace hydrogen additions in affecting mechanical properties was assessed using electronic structure measurements. Fig. 6 shows the profiles for the core-level spectra of Zr 3d, Cu 2p, and Al 2p in H-free and H-alloyed Zr₆₄Cu₂₄Al₁₂; minor doping with hydrogen can be seen to lead a downward shift in the binding energy of each element, consistent with the same trends reported in our previous studies [73] for the Zr₅₅Cu₃₀Al₁₀Ni₅ alloy after hydrogen microalloying. The core-level binding energy provides a signature to reflect information about the local chemical and configuration environment of the constituting atoms [74]. The downward shift in binding energy indicates that the local binding of metallic bonds around H atoms become "softened". Based on Troiano's hydrogen-enhanced decohesion theory [75,76], it is



Fig. 5. Comparison of brittle vs. tough metallic glasses. The ratio of $I_{\beta'}/n$ vs. Poisson's ratio ν for various glassy systems ($\gamma_c = 0.1$). The dash lines denote the boundary between brittle and ductile alloys. Data extracted from Refs. [49,72].



Fig. 6. Electronic structure analysis. The XPS core-level and valence-band spectra of H-free and H-alloyed $Zr_{64}Cu_{24}Al_{12}$. The Fermi level E_F is indicated by dash-dot line. Each spectra was calibrated by binding energy of C 1s electrons (284.8eV).

plausible that the H 1s electrons transfer to the Zr 3d conductionband and hence enhance the repulsive force between the metallic ions, further weakening the binding energy of such Zr-Cu and Zr-Al pairs surrounding H atoms. Therefore, it is to be expected that minor additions of hydrogen could induce more easily activated "soft spots" in glassy systems to act as potential nucleation sites for shear bands. Additionally, the profiles for the valence-band spectra of H-free and H-alloyed $Zr_{64}Cu_{24}Al_{12}$ are also shown in Fig. 6. The valence band spectra are very sensitive to the changes in atomic arrangement [77]. After hydrogen microalloying, the electronic density of states at the Fermi level EF decreases, which will lower the free energy of the system [78]; the binding energy of valence-band shifts toward a higher value, which will strengthen the attractive Coulomb force between atomic nucleus and valence electrons, and thereby reduce the size of valence electron cloud [79]. All these changes bring about a more stable and compact hydrogenated monolithic BMG, consistent with positron annihilation lifetime spectroscopy results [23], which ultimately serves to create a more strengthened structural matrix.

4. Discussion

4.1. Atomic structure from simulations

Recently, Mahjoub et al. employed an ab initio MD analysis to discern the changes in the amorphous structure of the ternary Zr₆₄Cu₂₄Al₁₂ BMG after the incorporation of minor additions of hydrogen [80]; however, due to the small time scale and system size used in their ab initio MD calculations, their conclusions failed to elucidate the salient mechanisms underlying the seemingly contradictory mechanical performance of H-alloyed BMGs. Compared with ab initio MD simulations, we believe that classical MD with a reliable embedded-atom method potential is more suitable for exploring the relationship between structure and properties of glassy alloys [30]. As of today, some MD simulations can contain millions of atoms [81] and be within microsecond time scales [82–84], yet they are still well below the conditions present in real-world laboratory experiments on BMGs. Here we overcome these difficulties by conducting MD simulations in five independent groups of model glassy specimens (marked as S1-S5, as stated in Methods), with different dimensions and cooling rates, in order to deduce the experimental characteristics of the structural changes following hydrogen microalloying through simulation. To eliminate statistical error, we employ 100 atomic configurations to calculate averaged structural parameters.

Fig. 7a displays the resulting element-specific pair distribution functions $g_{\alpha\beta}(r)$ of specimens with different hydrogen content, which relate to the probability of finding an atom at a distance r away from a reference atom [30]. The $g_{\alpha\beta}(r)$ is defined as:

$$g_{\alpha\beta}(r) = \frac{L^3}{N_{\alpha}N_{\beta}} \left\langle \left(\sum_{i=1}^{N_{\alpha}} n_{i\beta}(r)\right) \middle/ 4\pi r^2 dr \right\rangle$$
(1)

where *L* is the box size, N_{α} and N_{β} are, respectively, the number of atoms of type α and type β , and $n_{i\beta}$ is the number of atoms of type β in the radius *r* to r + dr of spherical shells centered on the *i*th atoms of type α . Incorporating such minor amounts of hydrogen into glassy metals additionally has a marginal impact on the Cu-Cu, Zr-Cu and Zr-Zr pairs. Fig. 7b is an enlarged view for the first peaks of these pairs; unconventionally, after the addition of hydrogen, the Cu concentration in the first-neighbor shell of Cu is elevated, which acts to facilitate close-packed icosahedra. Moreover, due to the electron interactions between the Zr and H atoms, the presence of hydrogen alters the bond lengths of the Zr-Cu and Zr-Zr pairs; the increased bond length of the Zr-Cu pairs further exemplifies that hydrogen-enhanced decohesion can exist in Zr-Cu-based amorphous systems and cause a reduced local atomic packing efficiency around H atoms.

As illustrated in Fig. 7c, the mixing enthalpy of the Zr-H bonding pair is $-69 \text{ kJ} \text{ mol}^{-1}$, more negative than the other pairs [85], so that



Fig. 7. Distribution of element-specific pairs. (a) Partial pair-distribution functions $g_{\alpha\beta}(r)$ for the H-free (dashed line) and H-alloyed (solid line) samples in group S4. Vertical bars label the bond lengths of Zr-H and Cu-H pairs on the basis of the sum of tabulated atomic radii. The first peaks of the Cu-Cu, Cu-Zr and Zr-Zr pairs are highlighted in (b). The inset to (a) illustrates one distorted H-centered cluster (Cu: orange; Zr: grey; H: blue). The mixing enthalpy for the constituting atomic pairs in (c) Zr-Cu-H, (d) Zr-Cu-Al-H, and (e) Zr-Cu-Al-Ni-H systems; the units are kJ mol⁻¹. The dash-dot line highlights the asymmetry about the chemical interactions. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

the hydrogen atoms are inclined to locate in the sites mainly defined by Zr atoms that have a strong affinity to H shown in Fig. 7a. The calculated interatomic distance (bond length) between Zr and H, in keeping with the results from inelastic neutron scattering technology [86], is much shorter than the sum of their tabulated atomic radii. As revealed by experimental characterizations [87,88] and *ab initio* calculation [80], the shortened bond length of Zr-H can be attributed to the s-d electronic orbital hybridization between these two elements. Conversely, for Cu-H bonds, the average bond length is slightly longer than the sum of their tabulated atomic radii, distinctly larger than the Cu-H bond lengths in inorganic compounds [89]. Subsequently, the local structure around H will be highly distorted from the different affinity of the Zr-H and Cu-H pairs, as illustrated by the inset in Fig. 7a; this in turn results in the surrounding atoms having a high potential energy state, shown in Fig. 8. In comparison to the H-free material, the fluctuations in potential energy (i.e., dynamic heterogeneity) in the H-alloyed material are more severe and result in a more stable matrix along with local higher energetic sites that are attained after minor additions of hydrogen.

We should note that the details concerning the evolution of atomic structure after hydrogen microalloying, respectively derived from the simulations on the binary Zr-Cu system and the XPS analysis on the ternary Zr-Cu-Al (or quaternary Zr-Cu-Ni-Al)

system, are all in agreement. The concept of mixing enthalpy provides an effective way of understanding the many chemical-related issues in amorphous alloys [90-92]. Fig. 7c-e list the values of mixing enthalpy ΔH_{AB} for each atomic pair in these three systems [85]; the chemical interactions in each system follow the asymmetry distribution law. We calculated the mean chemical affinity ΔH_{chem} for these H-free and H-alloyed samples (Zr₅₀Cu₅₀, $Zr_{64}Cu_{24}Al_{12}$, and $Zr_{55}Cu_{30}Al_{10}Ni_5$), with the ΔH_{chem} values estimated by employing a weighted average method, $\Delta H_{chem} =$ $4\sum_{A\neq B}\Delta H_{AB}c_Ac_B$, where c_A and c_B are, respectively, the molar percentage of the elements A and B [85]. We find trace hydrogen additions synchronously increase the negative values of ΔH_{chem} for the three samples, with the absolute magnitude of difference remaining at $\sim 2 \text{ kJ} \text{ mol}^{-1}$. Therefore, results from the MD simulations on binary sample could be applicable to the complicated ternary or quaternary systems.

We next introduce Voronoi polyhedra to describe the coordination environment around each atom. From our previous study [51], according to the geometrical frustration of the coordination polyhedral, the atoms in MGs are classified into six species, denoted as different Roman numerals (I-VI); these are shown in Table 2. This approach provides a means to deduce the hidden order of atomic packing, termed "gradient atomic packing structure", within the nanometer-scale range of various glassy alloys. This approach gives



Fig. 8. Distribution about the potential energy of each atom. Thin slabs, with thickness equivalent to 2.5 Å (roughly the average atomic spacing), (**a**) from H-free sample, and (**b**) from H-alloyed sample (S1 group). Atoms are colored by the differences between potential energy of each atom and mean potential energy over the same atom type. Each dash ellipse in (**b**) highlight the ambient environment around H atom.

a ubiquitous pattern for the medium-range order, and even the extended order of the atomic arrangements, *i.e.*, the local structure in the amorphous state undergoes a gradual transition from loose stacking to dense stacking of atoms, followed by the gradient evolution of atomic performance. As such, the amorphous structure specifically comprises three discernible regions: solid-like (I atoms), transition (II and III atoms), and liquid-like (IV, V and VI atoms) regions. In addition, for Zr-Cu-based MGs, the most locally favored coordination polyhedra for Cu and Zr atoms is the Z12 full icosahedra (<0, 0, 12, 0>) and Z16 types (<0, 0, 12, 4>), respectively [93], so that the central atoms (solid-like) in these clusters primarily control the intensity of elastic matrix. A comparison of the proportion of the different types of atoms in the H-free versus the H-alloyed specimens is displayed in Fig. 9. From this figure, it is apparent that the fraction of the atoms in these different groups differs markedly after minor additions of hydrogen; specifically, in the H-alloyed samples there is a higher proportion of solid-like and liquid-like atoms and a corresponding lower fraction of transition atoms that they replace. Moreover, the fraction of atoms in each group is sensitive to the cooling rate, particularly the solid-like atoms. As a consequence, we conclude that contrary to the results from Mahjoub et al.'s ab initio MD simulations [80], hydrogen-

Table 2							

Classification of coordination polyhedra around each atom in amorphous alloys

alloyed BMGs, formed in laboratory experiments at several orders of magnitude lower cooling rates, should not only be enriched in liquid-like atoms (which are responsible for the plasticity in these alloys) but should also contain even more solid-like atoms (which are responsible for their strength), as compared to the corresponding H-free BMGs.

4.2. Spatial distribution of the liquid-like atoms

In many theoretical studies to date, the relationships between the topological local order and properties of certain MGs have been established in terms of their characteristic short-range order motifs within their amorphous structures, such as full-icosahedra or geometrically unfavorable polyhedra [30,34,93,94]. These approaches are powerful yet they can only provide a partial understanding as they neglect the role of medium-range order, they cannot determine the structural component of the "soft spots", and further fail to decouple the independent origins of the plasticity and strength of glassy alloys. In contrast, our "gradient atomic packing structure" model can provide a more complete description of these issues by delineating the precise nature of the "soft spots" as regions comprising liquid-like atoms and their neighbors.

CN ^b	Z clusters	Increasing content	VI			
	I	П	III	IV	V	
6	<0,6,0,0>					Non-Kasper clusters
7	<0,5,2,0>	<0,6,0,1>				
8	<0,4,4,0>	<0,5,2,1>	<0,6,0,2>			
9	<0,3,6,0>	<0,4,4,1>	<0,5,2,2>	<0,6,0,3>		
10	<0,2,8,0>	<0,3,6,1>	<0,4,4,2>	<0,5,2,3>	<0,6,0,4>	
11	<0,2,8,1>	<0,3,6,2>	<0,4,4,3>	<0,5,2,4>	<0,6,0,5>	
12	<0,0,12,0>	<0,2,8,2>	<0,3,6,3>	<0,4,4,4>	<0,5,2,5>	
13	<0,1,10,2>	<0,2,8,3>	<0,3,6,4>	<0,4,4,5>	<0,5,2,6>	
14	<0,0,12,2>	<0,1,10,3>	<0,2,8,4>	<0,3,6,5>	<0,4,4,6>	
15	<0,0,12,3>	<0,1,10,4>	<0,2,8,5>	<0,3,6,6>	<0,4,4,7>	
16	<0,0,12,4>	<0,1,10,5>	<0,2,8,6>	<0,3,6,7>	<0,4,4,8>	
17	<0,0,12,5>	<0,1,10,6>	<0,2,8,7>	<0,3,6,8>	<0,4,4,9>	
	Kasper (Polytetra	hedral) clusters				

^a Note that Roman numerals figure the atoms at the centers of corresponding coordination polyhedral, details can be found in Ref. [51].

^b Coordination number.



Fig. 9. Variation in the fraction of different kinds of atoms after hydrogen microalloying. Histogram displaying the fraction of the solid-like, transition and liquid-like atoms in simulated samples, respectively. Scale bar \equiv 10. Each group is scrutinized to extrapolate the trend in experimental BMGs, which is sensitive to the cooling rate. Error bars are standard deviations of the mean.

Accordingly, quantifying the fraction and spatial distribution of the liquid-like atoms can be used to derive the number of "soft spots" in any amorphous sample. In addition, the transition atoms can serve as an intermediary between the contrasting characteristics of the solid-like and liquid like atoms; indeed, the fraction of both these two kinds of atoms are increased with the addition of hydrogen, as shown in Fig. 9.

The spatial distribution of liquid-like atoms in both H-free and H-alloyed samples can be characterized in terms of a selfcorrelation coefficient c(r) and inhomogeneity parameter h, as presented in Fig. 10a. By employing the program OVITO [59], the coefficient c(r), normalized by covariance, is found to decay exponentially with respect to the distance r from a reference position, which can be fitted by the two-phase exponential decay function, $c(r) = c_0 + A_1 e^{-r/a_1} + A_2 e^{-r/a_2}$, where c_0 is an offset, A_1 (A_2) is the amplitude, and a_1 (a_2) is the decay constant. We find that there is only a subtle change in the correlation length of liquid-like atoms after incorporating a small amount of H atoms, *i.e.*, the average size of the liquid-like regions is nearly equal in H-free and H-alloyed samples.

We can define an inhomogeneity parameter *h*, which describes the extent of localization about the characteristic atoms, as:

$$h = \frac{1}{2N} \sum_{k=1}^{r} w^{1-k} \sum_{i=1}^{2^{3k}} \left| m_i - \overline{m} \left(2^{3k} \right) \right|$$
(2)

where *N* is the number of investigative atoms in the box, *w* is the weight factor whose value is about 8.89, m_i is the actual number of atoms in each grid, \overline{m} is the mean value of atoms calculated for 2^{3r} grids (for details, see Appendix in Ref. [95]), and the value of *r* was either taken as 5 or 6 so that each grid contains at most one atom. For the H-free and H-alloyed samples, the value of *h* calculated for the H-alloyed sample is relatively small, which corresponds to a lower localization around characteristic atoms. Combined with the results from Fig. 9, this implies that with the increased number of liquid-like atoms, with a similar correlation length and a more uniform distribution, in the H-alloyed samples, such hydro-BMGs will have more liquid-like regions, which correspond to "soft spots" (which promote deformability).

In Fig. 10b and c, we respectively select two slabs from the H-free and H-alloyed samples to map the two-dimensional spatial distribution of the solid-like, transition and liquid-like regions. For a direct comparison, the white circles superimposed on the contoured maps represent the anelastic atoms that emerge during shear deformation. The local minimum nonaffine displacement (D_{\min}^2) was adopted to identify the anelastic atoms (a threshold of 0.1 was selected for shear deformation) involved in the local irreversible rearrangement [96]. The D_{\min}^2 of the central atom *i* relative to its nearest neighbor atoms *j*, can be defined as [70]:

$$D_{i,\min}^{2} = \frac{1}{N_{i}} \sum_{j} \left\{ \overrightarrow{r_{j}}(t) - \overrightarrow{r_{i}}(t) - J_{i} \left[\overrightarrow{r_{j}}(t - \Delta t) - \overrightarrow{r_{i}}(t - \Delta t) \right] \right\}^{2}$$
(3)

where N_i is the total nearest neighbors of the *i*th atoms within the reference configuration, $\overrightarrow{r}_{i}(t)$ is the position of atom *i*th at time *t*, J_{i} is locally affine transformation matrix, and Δt is the time interval for the atomic rearrangement. Clearly, the fertile "soft spots" trigger more sites for STZs, which further weaken the strain localization generated during the deformation of the H-alloyed material. Moreover, the locations of hydrogen atoms are also mapped in Fig. 10c. As discussed in Refs. [15,16], Zhao et al. deduce that mobile H in hydrogenated Zr-based metallic glasses acts as a "spacer", to overcome the energy barrier for the nucleation of STZ, which further softens the local surrounding sites. Based on the above results, majority of H atoms in our microalloyed BMGs also belong to such mobile "spacers", because of the weak binding between the surrounding atoms with a higher energy state. In Fig. 10c, the mobile dispersed H atoms always reside within, or around, the liquid-like regions and, as such, act as the catalyst for the formation of "soft spots" in the H-alloyed samples, which are thus more mobile than the ones in the H-free material. We should note that a decreased fracture toughness was observed in Zr-based BMGs containing a high hydrogen content, exceeding 800 wt.ppm, from using the cathodic charging technique [97]; we believe that here the non-uniform fertile H atoms may cause the aggregation of liquid-like atoms, which can further degrade the number of "soft spots" to induce strain localization which serves to limit ductility and hence toughness.

4.3. Localization of STZs during deformation

To compare the details of the localization process of the STZs in the H-free and H-alloyed BMG samples, we employed large-scale three-dimensional simulations under uniaxial loading. Fig. 11a displays the resulting compressive stress-strain response



Fig. 10. Quantitative comparison of the "soft spots" in H-free and H-alloyed samples. (**a**) The self-correlation coefficient c(r) as a function of distance r for the liquid-like atoms in glassy alloys from group S1. The correlation length corresponds to the distance when the value of correlation coefficient decays to 0.02. The inhomogeneity parameter h of liquid-like atoms in each specimen is also marked in (**a**). Contoured maps showing the spatial distribution of atoms within different regions in slices of (**b**) H-free and (**c**) H-alloyed specimens. Each thin slab, with thickness equivalent to 2.5 Å (roughly the average atomic spacing), was randomly captured from the box along the *z*-axis. The white spheres superimposed on the maps denote the locations of anelastic atoms under pure shear loading to a strain of 5% before global yielding; each STZ is highlighted by dashed ellipse. The smaller green balls in (**c**) map the sites occupied by hydrogen atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

performed on the specimens from group S4. The changes in mechanical behavior predicted from these simulations are in good agreement with the experimental results, specifically the higher strength and higher yield strain for the H-alloyed BMGs. Both samples illustrate significant stress overshoot followed by an abrupt stress drop after yielding, which is a signature of substantial strain localization emerging in the form of a dominant shear band. During the compressive deformation, we chose $D_{\min}^2 = 1.0$ as the threshold to judge whether atoms are regarded as anelastic ones that have undertaken clear shear transformation or not. The number of anelastic atoms was monitored during the deformation and found to gradually increase with increasing strain, as plotted in Fig. 11b. Fig. 11c shows the distribution of anelastic atoms at three strain levels, i.e., 5, 6 and 7%, in the H-free and H-alloyed samples. In Regime A (\leq 6% strain), before the onset of yielding in the H-alloyed specimen, minor additions of hydrogen can help facilitate the proliferation of anelastic atoms to create a relatively uniform distribution, which implies that more "soft" sites for STZ activation exist in the hydrogenated alloys at the initial elastic (or inelastic) stage. Conversely, in Regime B (~6-8% strain), the yielded H-free sample now contains more anelastic atoms, yet appears to undergo marked strain localization in the central region of the sample. The slower strain concentration in the H-alloyed sample, associated

with its strengthened matrix ("backbones"), is deemed here to be responsible for the observed delayed yield (larger yield stress and strain) phenomenon. However, in Regime C (\sim 8–10% strain), which is well into the plastic flow region, there are now clearly more anelastic atoms distributed evenly in the H-alloyed sample. In general, these simulations show that minor additions of H can endow amorphous alloys with more sites which evolve into SB embryos, which in turn further weaken the degree of any strain localization during compressive deformation.

By contrast, glassy structures can rejuvenate more readily under tension than under compression loading, as more STZs can be distributed over the deformed samples [98]. Hence, in order to compare the deformability of H-free versus H-alloyed specimens, we performed simulated tensile tests on these alloys; results are illustrated in Fig. 12. Large differences in the degree of strain localization can be seen, the plasticity of hydrogenated alloy involving more incipient SBs to consume external energy during plastic flow. In turn, as the deformation progresses, the degree of strain localization becomes more intense in the H-free material leading to instability failure at a lower fracture strain than in the Halloyed sample.

To revisit the original question posed at the start of this paper on the origin of the transition from "strong-yet-brittle" to "stronger-



Fig. 11. Response to compression loading. (a) Representative compressive stress-strain curves of the H-free and H-alloyed samples in group S4. Vertical bars label the yield points. (b) Number of anelastic atoms as a function of the compressive strain at three deformation stages, respectively. (c) Projected views of the spatial distribution of anelastic atoms at three moments, selected from different stages in (b), respectively. Atoms are colored according to their the nonaffine displacement, D_{min}^2 .

and-tough" BMGs, as has been experimentally shown, for example, by 5 at.% Al additions to Cu₅₀Zr₅₀ [99], 8 at.% Ag additions to Cu₅₀Zr₅₀ [100] and minor H additions to Zr-Cu-based BMGs in the current work, the results of our experimental and simulation study are summarized in Fig. 13. At the fundamental level, the diverse relaxation dynamics caused by thermal activation are considered to be responsible for the different phases of strain localization during deformation; specifically, the β' -relaxation corresponds to the nucleation of STZs, the β -relaxation corresponds to the percolation of STZs, and the α -relaxation corresponds to the initiation of shear bands, which represents the essence of plasticity in BMGs. Based upon our above experimental and simulated results, the "strongerand-tough" H-alloyed glasses display intensive matrices (manifest as higher E_{α} and E_{β} energies for α - and β -relaxations, a more stable and dense structure, leading to a larger fraction of 'solid-like' atoms) and more, higher activity, "soft spots" (manifest as a higher $I_{\beta'}$, smaller *n*, lower β' -relaxation energy $E_{\beta'}$, a distorted and loose local configuration around H atoms, and a larger fraction and more uniform distribution of "liquid-like" atoms), all as compared to the corresponding H-free "strong-yet-brittle" alloys. Thus, as a consequence of imposing external energy to "stronger-and-tough" BMGs, the generation of more mobile "soft spots" creates more sites for the nucleation of STZs at relatively low stress levels; in turn, the latter percolation of STZs and corresponding initiation of SBs is impeded by the intensive matrixes in these alloys (with their stronger, stiff, "backbones"), which leads ultimately to a cascade of incipient SBs that generates their higher yield strengths. In summary, the structural origin of strength and toughness in glassy alloys can be described, in terms of the concept of a "gradient atomic packing structure", as an increased intensity of "backbones", which are responsible for their strength, and an increased number of "soft spots", which are responsible for the plasticity in these alloys, with both these features being synchronously achieved in the "stronger-and-tough" BMGs.

5. Conclusions

Comparative studies on H-free and H-alloyed Zr-Cu-based BMGs were performed using both experiments and dynamic numerical simulations. We observe an increase in strength, ductility and toughness in both experimental and simulated H-alloyed samples. With hydrogen microalloying, we attribute the higher strength to the elevated activation energy for α -relaxation and β -relaxation, which is intrinsically rooted in the increased number of "solid-like"



Fig. 12. Atomic configurations in response to tensile loading. Images of the atomic configurations during simulated uniaxial tensile loading, showing the distribution of strain localization and further growth of SBs captured from (a) H-free and (b) H-alloyed samples in group S3 at different levels of tensile strain. Atoms are colored according to their nonaffine displacement, D_{\min}^2 .

atoms which constitute the stiff "backbones" of the alloy's matrix structure. Moreover, the minor additions of hydrogen can decrease the activation energy but raise the intensity of β' -relaxation, together with an increased average number of anelastic atoms for the nucleation of STZs; this in turn creates more mobile "soft spots" in H-alloved specimens to promote shear banding, extensive plastic deformation and hence toughness. Specifically, based on our "gradient atomic packing structure" model, by incorporating hydrogen atoms into amorphous alloys, the number and even distribution of liquid-like atoms is also increased; furthermore, they develop more "soft spots" with higher distortion energy to be fertile sites for STZs, resulting in the mitigation of strain localization that finally improves the deformability. Note that this is also critical for the fracture resistance and damage-tolerance of BMGs; these alloys invariably possess high strength but the additional development of plasticity serves to enhance their fracture toughness. Indeed, certain BMGs, such as Pd-based glasses, display some of the highest combinations of tensile strength and fracture toughness for any material on record [5].

We believe that the insights into the fundamental origin of the mechanical properties of BMGs generated by the experimental and numerical studies in this work can provide practical guide-lines for the design of stronger, more plastic, and tougher amorphous metal alloys. Moreover, in this work, we employ the feature of β' -relaxation to semi-quantitatively evaluate the number of potential "soft spots" in amorphous alloys, which can be readily measurable experimentally. More importantly, we believe that the results of our research provide an essential, in-depth, correlation between the structure, relaxation behavior and mechanical properties of metallic glasses, which has not been realized in previous studies.

Data availability

The data that support the findings of this study are available from the corresponding author, specifically Professor Yanqing Su of the Harbin Institute of Technology (email: suyq@hit.edu.cn) upon reasonable request.



Fig. 13. Schematic illustration for the structural origins of the strength and toughness of BMGs. Comparison of the atomic response to mechanical or thermal agitations between "strong-yet-brittle" (upper panel) and "stronger-and-tough" (lower panel) BMGs. The white spheres superimposed on the maps denote the anelastic atoms emerged during these processes.

Conflicts of interest

The authors declare no competing interests.

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Appendix A. Supplementary data

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