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Effect of hydrogen on the yielding behavior and shear transformation zone volume in metallic glass ribbons

Yakai Zhao^a, In-Chul Choi^a, Moo-Young Seok^a, Min-Hyun Kim^{b,c}, Do-Hyang Kim^c, Upadrasta Ramamurty^{d,e}, Jin-Yoo Suh^{b,*}, Jae-il Jang^{a,*}

^a Division of Materials Science and Engineering, Hanyang University, Seoul 133-791, Republic of Korea

^b High Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

^c Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Republic of Korea

^d Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India

^e Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589, Saudi Arabia

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Abstract

The effect of hydrogen (H) charging on the shear yield strength (τ_{max}) and shear transformation zone volume (Ω) of Ni–Nb–Zr metallic glass ribbons, with varying Zr content, were studied through the first pop-in loads during nanoindentation. Weight gain measurements after H charging and desorption studies were utilized to identify how the total H absorbed during charging is partitioned into mobile and immobile (or trapped) parts. These, in turn, indicate the significant role of H mobility in the amorphous structure on the yielding behavior. In high-Zr alloys, τ_{max} increases significantly whereas Ω decreases. In low-Zr alloys, a slight decrease in τ_{max} and increase in Ω were noted. These experimental observations are rationalized in terms of the mobility of the absorbed H in the amorphous structure and the possible role of it in the shear transformation zone dynamics during deformation of the metallic glass. © 2014 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Amorphous alloys; Hydrogen; Nanoindentation; Yield behavior; Shear transformation zone (STZ)

1. Introduction

Since the discovery of amorphous alloys by Klement et al. [1], there has been considerable interest in these materials due to their unique properties and functionalities, including their potential as an effective hydrogen (H) storage and separation medium [2,3]. Recently, metallic glass (MG) membranes that are permeable to H have gained interest due to the increasing importance of H separation in a number of applications, e.g., H-powered fuel cells. In particular, MG-based membranes are considered as an attractive replacement for expensive Pd and Pd-based alloy membranes because of their comparable H permeability but lower cost [4,5]. In addition to such technological importance, the possible influence of H on the structural characteristics of MGs has also gathered scientific interest due to the small size of H and the open interatomic spaces in the amorphous structure [6,7].

Generally, the compositions of MGs that are suitable for H separation have hydride-forming elements such as Zr and Ti due to their strong affinity to H. A representative example is the Ni–Nb–Zr alloy system in which Zr is the key element [8,9]. It has been reported that with increasing Zr content in this system, the interatomic spacing, H solubility and diffusivity increase whereas the crystallization temperature (T_x) , hardness and fracture strength decrease

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^{*} Corresponding authors.

E-mail addresses: jinyoo@kist.re.kr (J.-Y. Suh), jijang@hanyang.ac.kr (J.-i. Jang).

[5,10,11]. Additionally, pronounced H embrittlement (HE) was also reported in alloys with high Zr content, which seriously compromises the utility of MGs in the intended application. Consequently, excellent resistance to HE is one of the primary requirements for MG-based H selective membranes.

In crystalline metals and alloys, the influence of H on the mechanical behavior (including HE) has been a subject of extensive studies over the past century [12-15]. Since deformation mechanisms in MGs are completely different from those in crystalline alloys [16-19], the mechanisms utilized to rationalize the H effects on mechanical properties in crystalline metals may not be applicable to those in MGs. While the mechanical behavior of hydrogenated MGs is investigated to some extent [20-22], no attempt to examine the influence of H on the yield behavior of amorphous alloys has been made until now. In this study, towards this end, we examine the spherical-tipped nanoindentation responses of a series of MG alloy ribbons that have varying Zr contents. The influence of H on the first pop-in load, P_I , and in turn the maximum shear yield stress underneath the indenter, τ_{max} , was examined [23,24]. Statistical analysis of the τ_{max} data was utilized to estimate the volume of the shear transformation zone (STZ), Ω , and how it is influenced by the H absorption in the alloys with different Zr content in the alloy. Our results show that the mechanical response of hydrogenated MGs is sensitive to the Zr content in them. These were then coupled with the results of the H desorption experiments to discuss the mobility of absorbed H in the amorphous structure and on local structural packing.

2. Experimental

Melt-spun MG ribbons, \sim 30–60 µm thick, with the compositions (in at.%) of $Ni_{45}Nb_{30}Zr_{25}$, $Ni_{33}Nb_{22}Zr_{40}Co_5$, Ni₂₇Nb₁₈Zr₅₀Co₅ and Ni₃₅Nb₃₀Zr₁₅Ti₁₀Fe₅Co₅, were prepared. These alloy compositions were selected on the basis of the $(Ni_{0.6}Nb_{0.4})_{100-x}Zr_x$ scheme, which has been shown to combine high H permeability and mechanical stability [5,11], and are hereafter referred to as Zr_{25} , Zr_{40} , Zr_{50} and Zr₁₅Ti₁₀, respectively. In the latter two, 5 at.% Co is added as it suppresses severe HE that commonly occurs in high-Zr alloys [11]. Note that in $Zr_{15}Ti_{10}$, the Ti content was also used for the abbreviation since Ti also exhibits a strong affinity to H just as Zr [8]. Samples with an area of $\sim 50 \times 10 \text{ mm}^2$ were cut from the ribbons and one side of them was coated with a $\sim 150 \text{ nm}$ thick pure Pd via RF magnetron sputtering. The purpose of this catalytic layer is to enhance the surface kinetics for the dissociation/recombination of H molecules during charging. Subsequently, H charging was performed in a Sievert-type apparatus at 300 °C and under constant pressure (0.5 MPa) of gaseous H₂ for 3600 s, followed by waterquenching of the specimen-containing cylinder. The alloys were weighed before and after charging for estimating the mass fraction of H in each sample. While the specimens weigh ~100 mg and the weight change due to hydrogenation is ~1 mg, the precision balance, MSE3.6P-000-DM (Sartorius, Göttingen, Germany), can weigh with the resolution of μ g, leading to an accuracy of 0.001% in weight gain measurement.

Nanoindentation tests were conducted at room temperature using a Nanoindenter-XP (formerly MTS; now Agilent, Oak Ridge, TN, USA) with a spherical indenter (tip radius, $R = 5.73 \,\mu\text{m}$) on the side of the sample surface that was not coated with Pd and was polished with 0.3 µm alumina to a mirror finish. Prior to testing, R was calibrated through the Hertzian contact analysis [25,26] of indentations made on fused quartz. About 50 tests for each condition were conducted in load-control mode at a constant loading rate of $dP/dt = 1 \text{ mN s}^{-1}$, where P is the indentation load and t is time. In every case, the maximum depth of penetration (h_{max} , at largest ~400 nm) was much lower than one-tenth of the ribbon thickness. Hence, the effect of the substrate on the measured P vs. depth of penetration, h, can be neglected. All H-charged specimens were tested within 72 h of charging.

For investigating the correlation between Zr contents and H solubility in the ribbons, H desorption behavior was analyzed by thermal desorption spectroscopy (TDS) studies with a thermal conductivity detector (TCD). For TDS measurements, AutoChem HP model 2950 Chemisorption Analyzer (Micromeritics Instrument Corporation, Norcross, GA, USA) was used. The flow rate of Ar carrier gas was 50 ml min^{-1} and the H release behavior was monitored during heating with a constant heating rate of $20 \,^{\circ}\text{C min}^{-1}$.

3. Experimental results

3.1. Estimation of critical shear yield stress

The *P*-*h* curves often exhibit either sudden bursts of displacement or load drops, when nanoindentation is performed under load or displacement control, which are often referred to as "pop-ins" [17,18,27,28]. If a spherical tip is used, the deformation prior to the first pop-in is purely elastic and hence follows Hertzian contact theory [26]. The first pop-in then corresponds to the elastic-to-plastic transition, and the load, P_I , at which it occurs can be utilized to compute τ_{max} , which represents the critical shear strength for the onset of plasticity, as [25]:

$$\tau_{\rm max} = 0.31 p_0 = 0.31 \left(\frac{3}{2} p_m\right) = 0.31 \left(\frac{6E_r^2}{\pi^3 R^2} P_I\right)^{\frac{1}{3}} \tag{1}$$

where p_0 and p_m are maximum and mean pressures of the contact, respectively, and E_r is the reduced modulus that can be determined by $E_r = \left(\frac{E_s}{1-v_s^2} + \frac{E_i}{1-v_i^2}\right)^{-1}$, where *E* and *v* are the elastic modulus and Poisson's ratio, with the subscripts *s* and *i* indicating the sample and the indenter, respectively.

Fig. 1 shows representative examples of the P-h curves with pop-ins. When the peak load was lower than the P_I



Fig. 1. Representative load, P, vs. depth of penetration, h, curves of (a) low-Zr alloys and (b) high-Zr alloys. "UC" and "C" indicate uncharged and charged alloys, respectively. The open circle data represent the fully elastic P-h responses obtained at a lower peak load (=10 mN).

(see the cases of blue open circle), the loading and unloading segments of the P-h curves completely overlap, with no residual indentation depth whatsoever, which indicates that the deformation is indeed as per the Hertzian contact theory. Also the experimental P-h data follow the Hertzian curves until the first pop-ins take place, validating that the "first" pop-in is indeed corresponding to the elasticto-plastic transition.

The cumulative distribution of estimated τ_{max} is illustrated in Figs. 2 and 3 summarizes the variation of τ_{max} as a function of the Zr content in the alloy for both uncharged (UC) and charged (C) alloys. In the UC samples, τ_{max} remains invariant at ~4 GPa for Zr₁₅Ti₁₀ and Zr₂₅ alloys; increasing the Zr content further leads to a linear reduction in τ_{max} . The values of τ_{max} upon charging are lower for Zr₁₅Ti₁₀ and Zr₂₅ alloys whereas they are higher than the corresponding UC values for Zr₄₀ and Zr₅₀ alloys. This is illustrated through a plot of the difference in C and UC values of τ_{max} in Fig. 3. It shows that H-charging increases the plastic flow resistance of higher Zr containing alloy in a significant manner. For example, τ_{max} nearly doubles upon charging the Zr50 alloy. In contrast, when



Fig. 2. Cumulative probability distributions of the maximum shear stresses at first pop-in loads for the (a) $Zr_{15}Ti_{10}$, (b) Zr_{25} , (c) Zr_{40} and (d) Zr_{50} alloys in both uncharged and charged conditions. Note that the axis scales of each figure are different from each other.



Fig. 3. The maximum shear stress (τ_{max}) at the first pop-in in uncharged (UC) and charged (C) alloys, and their difference ($\tau_{max(C)} - \tau_{max(UC)}$). The data of $Zr_{15}Ti_{10}$ are identified as "+ Ti_{10} ".

the Zr content is 25 at.% or lower, the plastic flow resistance actually decreases upon charging.

3.2. Measurement of H content

The mass fraction of total H amount absorbed after the charging operation was estimated as the weight gained by the specimen due to H charging, and is listed in Table 1. where it is clear that with increasing Zr content, the weight gained increases. Further analysis of the effects of Zr content on H was carried out through TDS studies. Fig. 4 shows the TDS spectra acquired during heating of constant rate, 20 °C min⁻¹, up to 700 °C. In Fig. 4a, the TCD signal represents the instantaneous partial pressure of H desorbed from the alloys. Thus, at any given temperature, a stronger signal indicates a larger amount of H desorption. Qualitatively. H desorption at higher temperatures corresponds to larger binding energy between H and surrounding metallic atoms [29]. At temperatures higher than \sim 500 °C, only Zr₄₀ and Zr₅₀ exhibit TCD signals, which also include sharp peaks.

Fig. 4b shows the variation in the integrated TCD data with temperature, which represents the total amount of H that is desorbed from the specimen during heating. The desorbed H amounts are similar in for all samples up to \sim 350 °C. At temperatures higher than \sim 350 °C, however, the integrated TCD signal increases with increasing Zr content. This trend of the saturation values of the integrated-TCD curves, which are listed in Table 1, is in agreement with those of total H amount measurement directly by weight change (also shown in the first column of Table 1).

In Fig. 4b, the T_x of each alloy is indicated with an arrow. Interestingly, the H desorption process is complete below T_x for $Zr_{15}Ti_{10}$ and Zr_{25} ($T_x = 519$ and $531 \,^{\circ}C$, respectively) whereas the saturation start temperatures are higher than T_x for Zr_{40} and Zr_{50} ($T_x = 490$ and $468 \,^{\circ}C$, respectively). The latter implies that H release continues to occur at temperatures higher than T_x . This, in turn, confirms that the H released at the sharp peaks is due to the dissociation of the crystalline hydrides with high Zr fraction [29].

4. Discussion

Results of the nanoindentation experiments in Section 3 clearly demonstrate that the effect of H on the plastic deformation behavior is sensitive to the Zr content in the alloy whereas the TCD experiments indicate that the chemical/ structural state of the absorbed H is also sensitive to the Zr content. These observations suggest that the influence



Fig. 4. Plots of (a) TCD signal and (b) integrated TCD signals acquired by TDS measurements of the charged alloys. The arrows represent the T_x values of the respective alloys.

of H on τ_{max} of the MGs, observed in Fig. 3, may be closely related to the solubility and mobility of H in the amorphous alloys. Below, we discuss these aspects in detail.

4.1. Mobile H vs. immobile H

In Fig. 4, while Zr_{25} and $Zr_{15}Ti_{10}$ alloys exhibit only one broader TCD peak at low temperatures (~170–210 °C) with an extended tail, Zr_{40} and Zr_{50} alloys show a broad peak at low temperatures and an additional sharp peak at high temperatures. Similar two-peak H desorption events at low and high temperatures were reported in Araki

Table 1

Amounts of total H (first column), mobile H (third) and immobile H (fourth) with the saturated values of integrated TCD signal (second).

			-	
Alloy	Total H content (wt.%) (by weight change)	Saturated values of integrated TCD signal (a.u.)	Estimated mobile H content (wt.%)	Estimated immobile H content (wt.%)
Zr ₁₅ Ti ₁₀	0.66	7.5	0.28	0.38
Zr ₂₅	0.84	8.2	0.27	0.57
Zr_{40}	1.12	11.2	0.28	0.84
Zr ₅₀	1.38	16.6	0.29	1.09

et al.'s work on Ni–Zr binary MGs [29]. The H desorbed at low temperature reflects the release of weakly bound mobile H within the amorphous structure whereas the high-temperature desorption is associated with strongly trapped (and hence) immobile H, and only the former can diffuse at room temperature [29–31].

In this context, it is noteworthy that the mobility of an H atom in a material is determined by its chemical environment, in terms of the nature of the neighboring atoms in the structure it experiences. It has been conclusively shown that the polyhedral interstitial sites (mostly tetrahedral sites [3,32]) surrounded by the maximum number of early transition metal (ETM) atoms (e.g., Ti, Zr) that have a strong affinity to H, are preferentially occupied by H atoms in an amorphous structure [2,33,34], i.e., H first occupies these sites, and only when in excessive goes to the other locations. Thus, a larger amount of immobile H can be expected in higher-Zr containing MG alloys as they are likely to have more number of Zr-rich sites.

Further quantitative analysis of the relative amounts of mobile and immobile H is made below with the aid of known H transport properties. One of the major parameters that defines these properties is the solubility constant, K, which is given by the ratio of permeability, Q, to diffusivity, D (K = Q/D). Then, the H concentration C (in mol m⁻³) can be experimentally determined as [33]:

$$C = K\sqrt{p} \tag{2}$$

where p is the applied H pressure (=0.5 MPa in the current work). In a previous study made on the same Ni-Nb-Zr MG system [8], permeation tests reveal that K remains invariant at $\sim 16 \text{ mol m}^{-3} \text{ Pa}^{0.5}$ with temperature in all the alloys examined. Since Q and D in these tests are only associated with the mobile H, C would represent the concentration of it. From C, the amount of mobile H (in wt.%) in charged specimens was estimated, and is listed in Table 1 (third column). All the four alloys examined in this work contain similar amounts of mobile H irrespective of Zr content, which is expected in view of the similar K[8]. Table 1 also provides the amount of immobile H that can be estimated as the difference between the total and mobile H contents, and the amount certainly increases with the Zr content. Reasonably good correlation between the H-induced τ_{max} change (Fig. 3) and the amount of immobile H (Table 1) leads us to deduce that the τ_{max} change may be mainly determined by the amount of immobile H rather than that of mobile H.

4.2. Hydrogen-induced change in STZ size

Statistical analysis of τ_{max} data is performed to estimate the size of STZs, and in turn examine the effect of hydrogenation on it. Based on the thermally activated, stressassisted behavior of STZs, in an earlier study we have suggested a way to estimate the STZ size as a function of the strain rate [17,18], of which a brief summary is presented below. In the cooperative shear model (CSM) model of Johnson and Samwer [35], yielding is determined by the cooperative shear motion of STZs and hence intrinsically depends on activation volume V^* . By differentiation of the activation energy in the CSM model, the relation between the STZ volume, Ω , and V^* can be obtained as:

$$\Omega = \frac{\tau_{C0}}{6CG\gamma_C^2 \zeta \left(1 - \frac{\tau_{CT}}{\tau_{C0}}\right)^{\frac{1}{2}}} V^*$$
(3)

where G is the shear modulus, τ_{CT} and τ_{C0} is the threshold shear strength at T and 0 K, respectively, and constants $C \approx 1/4$ and $\zeta \approx 3$ [35]. γ_C is the critical shear strain $(=\tau_{CT}/G)$ that can be related to the flow stress, through the scaling law, $\gamma_C = \gamma_{C0} - \gamma_{C1} (T/T_g)^M$, where $\gamma_{C0} = 0.036 \pm 0.002$, $\gamma_{C1} = 0.016 \pm 0.002$ and $M = 0.62 \pm 0.2$ [35]. Therefore, for a given G and T_g (glass transition temperature), both τ_{CT} and τ_{C0} (that is $\gamma_{C0}G$ at T = 0 K) can be estimated. Note that although T_g of each alloy is required here, we used the crystallization temperature, T_x , instead of T_g in the above analysis because the glass forming ability of the alloys examined is marginal and hence only T_x (provided in Section 3.2) could be measured reliably.

Thus, if V^* of the pop-in event can be estimated through nanoindentation tests, the volume of STZ involved in the yielding can be determined according to Eq. (3). As suggested by Schuh and Lund [36] and Schuh et al. [37], the cumulative distribution of τ_{max} , f (shown in Fig. 2), can be described as a function of the shear stress beneath the indenter, τ :

$$\ln[\ln(1-f)^{-1}] = \left\{\frac{\Delta F^*}{kT} + \ln\left[\frac{kT}{V^*(d\tau/dt)}\right]\right\} + \left(\frac{V^*}{kT}\right)\tau \quad (4)$$

where kT is thermal energy (k is the Boltzmann constant, T is the temperature), γ_0 is the attempt frequency (that is, the frequency of the fundamental mode vibration along the reaction pathway) and ΔF^* and V^* are the Helmholtz activation energy and volume of the event, respectively. Note that $(d\tau/dt)$ is a constant for nanoindentation tests conducted at a fixed loading rate of dP/dt. Therefore, at $\tau = \tau_{max}$, V^* can be estimated from the slope of $\ln[\ln(1-f)^{-1}]$ vs. τ_{max} plot, as shown in Fig. 5 where the tails of the distribution are excluded (so as to obtain representative values that are not dominated by the tail values). The correlation factor (R^2) for every case of the linear fittings in the Fig. 5 is higher than 0.95. Table 2 lists the values of V^* . It is noteworthy that Packard et al. [38] reported that in a Pd- and a Fe-based BMG the τ_{max} are independent of loading rate, and suggested that the distribution of the τ_{max} originates from scattering in the local atomic structure rather than thermal fluctuations, which implies that Eq. (4) may not be appropriate for estimating V^* of amorphous alloys. However, in our previous study on a Zr-based BMG [17], detectable rate dependency of the pop-in stress exists, indicating that, with the inherent inhomogeneity of the atomic configuration in the amorphous state, thermal fluctuation could still have a role to



Fig. 5. Linear fits to the $\ln[\ln(1 - f)^{-1}]$ vs. τ_{max} data, employed to estimate the STZ size, of (a) $Zr_{15}Ti_{10}$, (b) Zr_{25} , (c) Zr_{40} and (d) Zr_{50} alloys in both uncharged and charged conditions. Note that the axis scales of each figure are different from each other.

Table 2 Estimated activation volume, V^* , and STZ volume, Ω , of the alloys.

Alloy	Activation volume, V^* (nm ³)		STZ volume, Ω (nm ³)	
	Uncharged	Charged	Uncharged	Charged
Zr ₁₅ Ti ₁₀	0.0100	0.0125	0.219	0.272
Zr ₂₅	0.0146	0.0151	0.318	0.330
Zr_{40}	0.0212	0.0124	0.465	0.272
Zr ₅₀	0.0234	0.0156	0.514	0.343

play in the pop-in event. Therefore, it is likely that the rate dependency of the first pop-in event depends on the BMG composition (and thus structural conditions such as the kinetics of structural relaxation), although detailed reasons for the difference are an unresolved issue at this point. In the present study, tests on a selected MG (Zr_{50}) also exhibited a clear rate dependency of τ_{max} (see Fig. 6), convincing us that Eq. (4) can be applicable here.

By combining V^* with τ_{CT} and τ_{C0} , Ω values are determined according to Eq. (3) and are summarized in Table 2. From Table 2, a striking contrast in the H-induced



Fig. 6. Cumulative probability distributions of τ_{max} (for Zr₅₀) at three different loading rates.

change in Ω is observed for the alloys with different Zr contents – similar to that of τ_{max} . While hydrogenation enhances – but only slightly – the value of Ω estimated for $Zr_{15}Ti_{10}$ and Zr_{25} , it significantly reduces Ω in Zr_{40} and Zr_{50} .

4.3. Mechanism of the H effect on the yielding behavior

The Zr-content sensitivity of the H effect on τ_{max} and Ω may be rationalized by the different roles of the weakly bound "mobile" H and strongly bound "immobile" H in amorphous structure; i.e., while the mobile H would diffuse readily, the immobile H belongs to a trapped state. Strong binding of immobile H with the surrounding metallic atoms (mostly Zr) leads to the formation of densely packed structures that have specific chemical and geometrical configurations, which can have either hydride-like short range order or partially crystallized hydride phases [39]. In any case, the dense packing restricts the local atomic movement and consequently initiation of plastic deformation through STZ activation becomes difficult [20,39,40].

On the other hand, mobile H atoms may reduce the yield strength of MGs in two possible ways, both of which are analogous to that used for crystalline materials. First, they can act as a simple "spacer" in the interstitial site, which may occur in a somewhat similar way to "elastic shielding" for H-induced softening in crystalline alloys [13,15]; i.e., it enhances the interatomic spacing without any significant interaction with the surrounding atoms. One may expect in consideration of popular deformation mechanism of MGs that the mobile H atoms as "spacers" can either reduce the activation energy for STZs due to the weakened binding force between metallic atoms or ease the local atomic jump through the enhanced interatomic space. Second, the role of mobile H is also somewhat analogous to a term "defactants" (DEFect ACTing AgeNTS) that has been recently suggested as a new thermodynamic way to explain the H-enhanced local plasticity (HELP) in

various crystalline alloys; i.e., H atoms segregating at defects play roles as "defactants" that lower the formation energy of defects such as dislocation loops, resulting in HELP and thus HE [23,24,41]. Similarly, H atoms may thermodynamically reduce the formation energy of shear transformation zone although detailed mechanism is not fully understood at this point.

As mentioned above, the strengthening by H in the high-Zr alloys can be attributed to the formation of immobile H clusters. It should be pointed out that the immobile H clusters also exist in the low-Zr allovs but most likely with weaker binding energy and lower number density than those in high-Zr alloys, as schematically illustrated in Fig. 7a and b. As discussed earlier, the quantity of immobile H scales with the Zr content in the alloy whereas the mobile H content remains nearly invariant. On this basis, it is reasonable to assume that the yielding behavior of high-Zr-containing alloys is likely to be governed by the immobile H clusters that are omnipresent, as depicted in Fig. 7a. In the alloys with lower Zr content (Fig. 7b), in contrast, the number density of the immobile H clusters is not enough to influence the yielding behavior and, instead, the mobile H dominates, which results in a marginal reduction in the τ_{max} .

Turning attention to Ω , earlier studies suggest that it is determined by the relative degree of disordering of the amorphous structure [18], which is inherently inhomogeneous with wide distribution of energy states at the nano-scale [42,43]. This is schematically illustrated (solid lines)

in Fig. 7c and d. The width of the distribution reflects the relative homogeneity of the amorphous structure, i.e., the narrower the distribution, more homogeneous is the structure. A more uniform structure might be able to engage a greater number of atoms into collective movement in responding to the external stimulus (stress), the distance in which strains are accommodated (that should be approximately the same as Ω) increases [18]. Collectively, a narrower energy distribution in Fig. 7c and d corresponds to a larger Ω . Note that amongst all the possible atomic configurations, loosely packed regions that have higher local free volume content – and hence have higher potential energies – are the ones that are likely to activate STZs upon stressing [16].

With this background, H-induced changes in Ω can be rationalized as following. Flores et al. [21] reported that the free volume in Zr-based amorphous alloys is preferentially surrounded by a higher fraction of Zr atoms; i.e., the loosely packed volumes within the amorphous structure (having higher local free volume concentration as well as higher potential energy, as mentioned above) is expected to be Zr-rich. Thus, it is reasonable to expect a larger number of high energy Zr-rich sites in the high-Zr alloys (Zr₄₀ and Zr₅₀). Upon hydrogenation, H would go preferentially to these sites – because of the availability of the free volume – and in turn gets trapped. This results in a relatively greater number of densely packed structures with lower potential energy overall, as depicted by the leftward arrows in Fig. 7c. On the other hand, the clusters with lower



Fig. 7. A schematic illustration of the local structure of (a) high- and (b) low-Zr alloys in H-charged condition and relative changes in potential energy distribution caused by H in (c) high- and (d) low-Zr alloys.

potential energy, which have less Zr coordination, are mostly unaffected by H. Nevertheless, their potential energy can indeed slightly move to higher energy levels upon charging due to the lattice expansion caused by the mobile H, which acts as a spacer, as illustrated by the rightward arrows in Fig. 7c. Overall, especially due to the wide diversity of the H-induced structural change in high-Zr alloys (Zr_{40} and Zr_{50}), the width of energy distribution in the hydrogenated alloys would be expected to increase, as in Fig. 7c, implying a more inhomogeneous structure and thus a smaller STZ volume than that of the uncharged condition. Considering the inhomogeneous structure as depicted in Fig. 7a, it is conceivable that Ω is heavily affected and thus shrinks by the formation of immobile H clusters at the nanoscale.

In low-Zr alloys ($Zr_{15}Ti_{10}$ and Zr_{25}), the behavior of H is basically the same as that for the high-Zr cases described above, except a few important differences. As suggested by the TDS results given in Fig. 4a, the formation of the H-induced clusters in these alloys is likely to be relatively insignificant vis-à-vis that in high-Zr alloys in terms of binding strength and number density. Therefore, it is reasonable to infer that the reduction in the potential energy landscape in the low-Zr alloys due to hydrogenation and cluster formation (see the leftward arrows in Fig. 7d) is less than that in high-Zr alloy. As a result – and since the effect of mobile H is approximately similar in both low- and high-Zr alloys – the width of the potential energy distribution can be expected to get narrower for the charged low-Zr alloys, indicating that the structure becomes more uniform (see Fig. 7b and d). This offers a rationale as to why Ω increases slightly in $Zr_{15}Ti_{10}$ and Zr_{25} upon hydrogenation.

Before closing, it is noteworthy that in uncharged alloys, Ω increases with Zr content, indicating that the homogeneity may be improved by increasing the Zr content in the alloy. Indeed, it is obvious from Fig. 3 wherein the variability in τ_{max} data decreases with increasing Zr content for the uncharged alloys. This observation is also consistent with the results of the MD simulations conducted by Park et al. [44], which showed that increasing the Zr content in a CuZr binary amorphous system results in a concomitant increase in the internal energy and a reduction in structural disordering.

5. Conclusion

In summary, the effects of H absorption on the yield strength of four Ni–Nb–Zr amorphous metallic ribbons having various Zr contents were studied. Although the H absorption caused obvious change in the pop-in behavior and thus τ_{max} , such effect appeared differently in the alloys with different Zr content. While the τ_{max} increased in Zr₄₀ and Zr₅₀ alloys, a reduced τ_{max} in the Zr₂₅ and Zr₁₅Ti₁₀ alloys was observed. The H mobility in the amorphous structure significantly affects the mechanical behavior; i.e., the immobile H increases τ_{max} while the mobile H

decreases τ_{max} . The changes in STZ volume, calculated through cumulative analysis of pop-in, caused by H absorption were also found to depend on H mobility such that immobile H reduces the STZ volume while mobile H increases it. The reason was attributed to the relative homogeneity of the amorphous structure, discussed in terms of the local structure and potential energy distribution.

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