Hydrogen-induced softening and hardening of Zr-based amorphous alloy: dependence on the hydrogen content and mobility

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Abstract

The effects of hydrogen addition on the structural and mechanical properties of Zr_{57}Al_{10}Cu_{15.4}Ni_{12.6}Nb_{5} amorphous metallic alloy were analysed. Structural investigation, using x-ray diffraction, revealed that hydrogen addition causes the development of large void and structural expansion. By means of nanoindentation tests, it has been shown that hydrogen addition can induce either softening or hardening of Zr-based amorphous alloys depending on the extent of the hydrogen content and mobility. The shear softening of amorphous material is due to the weakness of atomic cohesion attributed to the squeezing of ‘mobile’ hydrogen atoms. When hydrogen content grows excessive, strongly bounded ‘immobile’ atoms form a densely packed structure that restrict the local atomic movement and consequently harden the amorphous material alloy.

1. Introduction

Hydrogen (H) separation and purification using metallic membranes is one of the principal methods of producing extremely pure hydrogen (99.9999%). Currently, the crystalline Pd-based metallic alloys are the industry-standard metallic membrane materials commonly used for hydrogen separation due to their high selectivity for hydrogen [1–7]. However, these alloys are too expensive and their performances are extremely reduced at low temperature and high pressure [8]. Therefore, it is essential to develop new alloy, which can circumvent the detriments of Pd-based alloys. Based on the literature review and industrial reports, the main technological requirements which the high-quality hydrogen purification metallic membranes have to satisfy are high hydrogen diffusivity, elevated permeability as well as a good immunity from hydrogen embrittlement [9]. Moreover, the separation and purification membranes must provide high hydrogen solubility and high diffusivity at the membrane surface. Actually, with the emergence of new advanced materials, several alternatives have been proposed to replace the limitations of crystalline Pd-based alloy membranes. One of the potential candidates is the amorphous metallic alloys because of their relative reduced cost, excellent mechanical and structural properties, higher hydrogen solubility compared to their analogues crystalline as well as high resistance to hydrogen embrittlement [1].

The objective of this work is to test and characterize new amorphous metallic membranes that exhibit performance approaching the existing crystalline Pd-based metallic membranes with a reduced cost and possible high resistance to hydrogen embrittlement. We intend to select samples of Zr-based amorphous metallic alloy and characterize their behaviour under hydrogen exposure, in order to obtain further information about their potential uses as separation membranes. The composition of amorphous metallic alloys is studied and the metallic elements are selected based on published data on various Zr-based amorphous alloys exhibiting good hydrogen permeation.

2. Alloy selection and samples preparation

Early Transition Metals (ETM) are the mostly used for the design of promising amorphous alloys that can demonstrate high hydrogen permeabilities [8]. For example, the Ni-based compositions are the most common
and generally combined with other elements such as Zr, P, Nb... Etc [10, 11]. The intent is to circumvent the hydrogen embrittlement and increase the functional temperature of the amorphous membranes (around 700 °C for membrane reactors) by increasing crystallization temperature of the designed amorphous metal. The addition of various alloying elements to amorphous basic alloys is very important and must be carefully selected based on various physical and structural considerations (diffusivity, solubility, temperature range. Etc). This is the target of many undergoing researches. Furthermore, Zirconium, due to its strong affinity to hydrogen, is the key element of composition alloys as it influences the kinetics of hydrogen transport [12, 13]. Jayalakshmi et al [9] have studied the properties of Ni–Zr–Nb–Ta amorphous metal after hydrogenation and they found that with increasing Zr content, the crystallization temperature decreased, demonstrating a close dependence of thermal properties on Zr content. Furthermore, the increasing Zr content in the Ni–Nb–Zr alloy system leads structurally to an open interatomic spacing whereas the crystallization temperature, hardness and the global strength decrease [14]. Furthermore, the increase of Nb content enables the latter system to increase its crystallization temperature [15]. It has been shown also that with the addition of both Ti and Hf in Pd-coated Zr–M–Ni alloy system, the permeability of the various metallic membrane compositions decreased due to the increase of the permeation activation energy. The effects of addition of other chemical elements like Ti, Mo, Ta, Co, Hf, Cu, and Al to the amorphous systems Ni–Zr, Ni–Nb, Cu–Zr and Ni–Nb–Zr have been extensively studied in order to improve their performances [16, 17]. The slight addition of Co is seen to reduce hydrogen embrittlement. The metal Ta has a very high melting point [16] and it is extremely permeable to hydrogen. Overall, a representative alloy system for membranes consists of the major elements: Zr, Ni, Nb, Co, Ta, and Ti. In this work, we have investigated a Zirconium-Copper based amorphous alloys as candidate for hydrogen purification membranes. These systems are identified to have compositional regions that enclose promising permeabilities similar to Pd [18]. Advanced simulations showed that the amorphous alloys systems based on the binary ZrCu- hold promise solubility and permeability as good as Pd/Pd-Ag metallic membranes. As a starting point in investigating the CuZr systems, the alloys ZrAlCuNiNb is chosen as a target composition.

2.1. Membrane samples preparation

Ingots of alloy ZrCuAlNiNb are prepared by arc melting the pure elements Zr (99.9%), Cu (99.99 mass%), Al (99.9 mass%), Ni (99.9 mass%), Nb (98.99 mass%) under Ti-purified Ar atmosphere. An appropriate amount of ingot is re-melted several times to ensure good homogeneity. Subsequently, after alloy preparation, the ingot is used to fabricate the amorphous membranes by means of a melt spinning technique [2, 19] at SIMaP Laboratory, Grenoble- France. The ingot is filled into quartz crucible under argon and placed above a rotating copper wheel in the melt spinner. The chamber containing the crucible and wheel is maintained under inert atmosphere throughout cycles of filling with argon and evacuating to primary vacuum (at ~10⁻³ mbar). The chamber is then exposed to high vacuum of minimum 10⁻⁶ Torr using an oil diffusion pumps. Once the wheel is rotating at 1000 to 2000 rpm, the induction coil heats the sample to the melt point of the alloy (Tm = 1250 K for Zr-based alloys). The melted alloy is then extruded onto a copper wheel through a small orifice of ~0.5 mm, which rapidly cools the alloy (~10⁶ °C s⁻¹) to produce a solid amorphous membrane ribbons having typical thickness of 30–70 μm depending on wheel rotation speed.

3. Hydrogen charging

Hydrogen was introduced into the specimens using a cathodic charging method in a 0.1 M NaOH solution. Before charging, the sample surface was gently polished with emery paper of 600 grades (in order to enhance the atomic hydrogen absorption [20]) and then immersed in the electrolytic solution. The set up for hydrogen charging is represented in figure 1. The hydrogen samples are loaded using two electrodes. The first ‘Ω’ is connected to the sample and the second is a cylindrical platinum ‘Ω’. A digital GBF ‘Ω’ of type ELC ALR3003D with frequency of 50 Hz and an ammeter ‘Ω’ are used to provide various current densities (in mA cm⁻²). The sample, which plays the role of cathode, is directly attached to the support ‘Ω’ and immersed in NaOH or H₂SO₄ solution ‘Ω’. The charging was made under a current density ranging from 0.5 to 30 mA cm⁻² for different charging time intervals in order to monitor the dissolved hydrogen content. The hydrogen charging tests were carried out in the mechanical engineering laboratory of Sousse (LMS)-Tunisia.

4. Structural characterization

Possible structural and phase characterization changes due to hydrogen charging were checked by conventional x-ray diffraction (XRD), (PAN alytical X’Pert ProMPD SIMaP-Grenoble, France). The diffractometer is set with copper lamp of 1800 W coupled with a Ni filter which permits the selection of the Kα radiation with
\[ \lambda = 0.15418 \text{ nm.} \]

Figure 2 shows the XRD patterns of the Zr57Al10Cu15.4Ni12.6Nb5 amorphous alloys samples after hydrogen charging at various charging conditions. No sharp diffraction peaks are observed in diffraction angles \( \theta \) ranging from 20 to 80°. This indicates that all alloys have a unique amorphous phase suggesting that the samples maintain the amorphous structure with no evidence of metal hydrides development or other crystalline phases.

Besides, the first halos characteristic of the amorphous phase is seen to shift to lower scattering angles. Figure 3 shows the evolution of the angle positions of the first prominent maxima versus charging time, obtained by fitting the upper half of the first diffraction peak with a suitable peak-type function (Lorentzian or Voigt function) as shown in the insert of figure 2.

The shift of the maximum position of the diffraction intensity to lower values was reported in others hydrogenated amorphous alloys and crystalline metals \([21–24]\) and it was attributed to the structural expansion...
due to the hydrogen addition. The evolution of the angle positions to the lower values continue even for long hydrogen charging time (i.e. for 8 h).

5. Micromechanical characterization

Mechanical properties of amorphous membranes are of significant importance. Indeed, these membranes are usually subjected to high pressures and consequently they require sufficient mechanical strength to endure these large pressures. Furthermore, while amorphous alloys are renowned to exhibit good mechanical strength, the absorption of hydrogen can lead to embrittlement and mechanical failure under various purification operating conditions. In this study, the nanoindentation method was used in the microdeformation display of materials under a multi-axial loading. This method provides an effective approach for the deformation study of amorphous membranes because of the limitation in size of the samples. In order to examine the influence of hydrogenation on nanomechanical properties, the sample surfaces were ground and gently polished with fine SiC paper and 0.3 μm alumina to a mirror finish and Nanoindentation performed on the alloy by Nanoindenter-XP (formerly MTS-SiMAP-Grenoble, France) equipped with continuous stiffness mode (amplitude 2 nm at 45 Hz). The displacement and load resolution are 0.1 nm and 50 nN respectively. In the experiment, Berkovich diamond indenter was employed. For the reproducibility of the obtained results, the experiments were repeated 5 times for each set of conditions with the error bars representing the 95% confidence interval of the mean. In all cases, the maximum depth of penetration (Hmax ∼ 500 nm) is much less than one-tenth of the ribbon thickness so that the effect of the substrate on the nanoindentation responses could be insignificant. Figure 4 shows typical nanoindentation load-displacement curves of Zr57Al10Cu15.4Ni12.6Nb5 amorphous alloy for the as-quenched, slightly (i.e. 1 mA-1 h) and highly (i.e. at 1mA-8h) hydrogenated samples at current density I = 1 mA cm⁻².

For slightly hydrogen charged specimens (i.e. 1 mA-1 h), the peak-load displacement is larger than that of the as-prepared sample, which implies that the low charged specimens have lower hardness (i.e. softer). However, for higher hydrogen charged specimens (i.e. at 1mA-8h), the peak-load displacement is seen to be lower than that of the as-prepared sample, which suggests that the high charged specimens have greater hardness (i.e. hardening). Figure 5 shows the evolutions in nanohardness of samples with different charging states (charging time, current density). The nanohardness values are estimated from the load displacement curves using the Oliver-Pharr method [25].

The nanomechanical behavior of amorphous metallic samples is predominantly affected by the extend of hydrogen addition. There are two notable trends exhibited in figure 5 as following: (1) the nanohardness decreases in Zr57Al10Cu15.4Ni12.6Nb5 amorphous alloy as the hydrogen is introduced with low content (i.e. for lower current density and short charging time). This indicate that slight content of hydrogen induces softening of the material; (2) the nanohardness increases in the subject alloy when hydrogen is introduced with high content (i.e. for higher current density and/or extended charging time) which suggests that higher hydrogen induces hardening instead of softening in this amorphous alloy. Other researchers have revealed that minor doping with hydrogen may improve the plasticity of Zr-based metallic glasses and attributed this plasticity to the
local atomic changes such as the local increase of free volume and the promotion of atomic rearrangement and flow ability \[26-29\]. The actual extended experimental observations suggest the existence of a threshold (critical value) of hydrogen content from which the amorphous material transits from softening to hardening. This threshold may explain the controversial published results on hydrogen hardening/softening effect in metallic glasses alloy systems \[30-32\]. The transition in the mechanical properties is a distinct physical phenomenon, suggesting a change of the character of material plasticity. It appears that on contrast to the high H-content degrading the mechanical properties of amorphous metallic alloys, a specific low range of H-content was observed beneficial. This controversial hydrogen effects have to be analyzed in light of the structural configuration of the considered amorphous alloy.

**6. Discussion**

As amorphous metallic alloys have disordered structures, the degree of dense packed atomic configurations in these alloys is obviously smaller than that in crystalline alloys and this structure offers more spaces and interstitial sites with different energies for hydrogen diffusion. Hydrogen tends to occupy a wide variety of

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**Figure 4.** Typical nanoindentation load-displacement curves of Zr_{57}Al_{10}Cu_{15.4}Ni_{12.6}Nb_{5} amorphous alloy before and after hydrogenation at distinct charging times (current density: \(I = 1 \text{ mA cm}^{-2}\)).

**Figure 5.** Variation in nanohardness for uncharged and hydrogenated Zr-based amorphous alloy at various charging sittings (i.e. hydrogen content).
interstitial sites depending on the structural configurations and the chemical compositions [33–35]. It will preferentially occupy the low-energy sites and once the H-content grows excessive, the high-energy sites will as well be occupied. From chemical concern, hydrogen atoms tend to bond with early transition metals (e.g. Ti, Zr), which have a strong affinity with hydrogen. It has been convincingly shown [36, 37] that when hydrogen atoms are slightly introduced in amorphous metallic alloy, they preferentially occupies an interstitial tetrahedral-like t sites and only go to octahedral-like and Zr- deficient tetrahedral-like o sites when in excess at high hydrogen loading. Furthermore, introduced hydrogen can be in ‘mobile’ or ‘immobile’ [37] states. The mobile H atoms, generally trapped by the local free volume, act mostly as a ‘spacer’ leading to interatomic spacing without causing strong binding with surrounding atoms. Gathering of more hydrogen may alter the local atomic configuration which in turn leads to higher lattice expansion with strongly bound immobile hydrogen atoms.

With this background, one may conclude that the hydrogen solubility (concentration) and mobility are the main reasons for the opposite trends of hardness changes illustrated in the experimental results of figure 5. The transition softening-to-hardening in amorphous metallic alloy can be rationalized as following: lower H content will be trapped in sites with low interatomic bounding and hydrogen is mobile within voids, in form of excess free volume. This may weaken the bounding force [38] and engage a greater number of atoms into collective movement and atomic jump capability in responding to an external stress. That explicitly, justifies the softening of material according to the well accepted deformation mechanism of amorphous alloys, highlighted by the shear transformation zone (STZ) and atomic jump free volume concepts [39, 40]. This interpretation is in harmony with the recent atomic-scale analysis carried out by Luo et al [41] where they showed that minor additions of hydrogen could induce an easily activated ‘soft spots’, involving most mobile atoms in glassy system which act as potential nucleation sites for shear bands. When the hydrogen content increases, extra H atoms will be trapped in other sites and strongly bound with surrounding metallic atoms (mainly Zr), forming a dense packed structure with complex chemical and geometrical configurations. This, results in the restriction of the local atomic movement that would ease the plastic deformation via the activation of the shear transformation zones (STZs). As consequence, material tends to a hardening. This dependence of softening-to-hardening transition on H content has been analogously reported in crystalline materials [42]. Small amount of hydrogen enhances the mobility of screw dislocation by reducing the Peierls potential [43] leading to material softening. With increasing hydrogen content, segregation of H-atoms to dislocations pin them and consequently increase the expected stress for plastic deformation, suggesting further hardening of material [44, 45].

In short before closing, the dual effect of H on the hardness of amorphous metallic alloy, observed in figures 4 and 5, may be closely related to the solubility and mobility of H in the amorphous metallic alloys due to their influences on the local atomic configuration and the potential energy distribution. Weakly bounded few ‘mobile’ H acts as simple ‘spacer’ that ease the local atomic rearrangement leading to the material softening. However, strongly bounded excessive ‘immobile’ H in amorphous structure leads to the formation of densely packed structures that restrict the local atomic movement and consequently, harden the amorphous material [46, 47].

7. Conclusion

Samples of Zr57Al10Cu15.4Ni12.6Nb5 amorphous alloys were electrochemically charged with hydrogen at various charging times and current densities. The structural and mechanical behavior of low-charged and highly-charged samples was systematically investigated through XRD and nanoindentation experiments. H-induced controversial nanohardness changes; decreasing and material softening by charging with low hydrogen concentration while increasing and material hardening if the hydrogen content grows excessive. The results of the hardening/softening behavior have been analyzed in term of internal parameters such as H-content, H-mobility and H-trapping sites.

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References

[1] Nishimura C, Komaki M, Hwang S and Amano M 2002 V-Ni$_{alloy}$ membranes for hydrogen purification J. Alloys Comp. 330–332 906–907

[2] Hoang H T, Tong H D, Gieles F C, Jansen H V and Elwenspoek M C 2004 Fabrication and characterization of dual sputtered Pd–Cu alloy films for hydrogen separation membranes Mater. Lett. 58 525

[3] Nishikawa M, Shiraiishi S, Kawamura Y and Takeishi T 1996 Permeation rate of hydrogen isotopes through palladium–silver alloy J. Nucl. Sci. Technol. 33 771–777

[4] Guo Y, Lu G, Wang Y and Wang R 2003 Preparation and characterization of Pt–Ag–ceramic composite membrane and application to enhancement of catalytic dehydration of isobutene Sep. Purif. Technol. 32 271–279

[5] Yamakawa K, Ege M, Ludescher B, Hirscher M and Kronmuller H 2001 Hydrogen permeability measurement through Pd, Ni and Fe membranes J. Alloys Comp. 321 17–23

[6] Yamakawa K, Ege M, Hirscher M, Ludescher B and Kronmuller H 2005 Hydrogen permeation through Pd/Fc/Fe and Pd/Fl multilayer systems J. Alloys Comp. 393 5–10

[7] Yamakawa K, Ege M, Ludescher B and Hirscher M 2003 Surface adsorbed atoms suppressing hydrogen permeation of Pd membranes J. Alloys Comp. 352 57–9

[8] Paglieri S N and Way J D 2002 Innovations in palladium membrane research Sep. Purif. Methods 31 1–169

[9] Jayalakshmi S, Choi Y G, Kim Y C, Kim Y B and Fleury E 2010 Hydrogenation properties of Ni–Nb–Zr–Ta amorphous ribbons Intermetallics 18 1988–93

[10] Strom-Olsen J, Zhao Y, Ryan D, Huai Y and Cochrane R 1991 Hydrogen diffusion in amorphous NiZr J. of the Less Common Metals 172/174 922–7

[11] Chin H S, Suh Y J, Lee W and Fleury E 2011 Hydrogen permeability of glass–forming Ni–Nb–Zr–Ta crystalline membranes Metals and Mater Inter 17 541–5

[12] Wang Y L, Suh Y J, Lee Y S, Shim J H, Fleury E and Cho Y W 2013 Direct measurement of hydrogen diffusivity through Pd–coated Ni-based amorphous metallic membranes J. Membr. Sci. 436 195–201

[13] Paglieri S N, Pal N K, Dolan M D, Kim S M, Chien W M, Lamb J, Chandra D, Hubbard K M and Moore D P 2011 Hydrogen permeability, thermal stability and hydrogen embrittlement of Ni–Nb–Zr and Ni–Nb–Zr–Ta–Zr alloy membranes J. Membr. Sci. 378 40–52

[14] Kimura H et al 2003 Thermal stability and mechanical properties of glassy and amorphous Ni–Nb–Zr produced by rapid solidification Mater. Trans 44 1167–71

[15] Dolan M, Dave N, Morpeth L, Donelson R, Liang D, Kellam M and Song S 2009 Ni-based amorphous alloy membranes for hydrogen separation at 400 °C J. of Membr Sci 326 549–55

[16] Yamaura S I and Inoue A 2010 Effect of surface coating element on hydrogen permeability of melt–spun Ni$_{40}$Nb$_{20}$Ta$_{5}$Zr$_{30}$Co$_{5}$ amorphous alloy, J. Membr. Sci. 349 138–44

[17] Sarker S et al 2016 Developments in the Ni–Nb–Zr amorphous alloy membranes Appl. Phys. A 122 168

[18] Sholl D S and Hao S 2011 Computational prediction of durable amorphous metal membranes for H$_{2}$ purification J. Membr Sci 381 192–206

[19] Dolan M D, Dave N C, Ilyushchkin A Y, Morpeth L D and McElman K G 2006 Composition and operation of hydrogen–selective amorphous alloy membranes J. of Membr. Sci. 283 30–55

[20] Eliazi N and Eliezer D 1999 An overview of hydrogen interaction with amorphous alloys Adv. Perform. Mater. 6 5–31

[21] Dandana W, Youshi M A, Hajlaoui K, Gamaoun F and Yavari A B 2017 Thermal stability and hydrogen–induced softening in Zr$_{50}$Al$_{20}$Cu$_{10}$Ni$_{10}$Nb$_{5}$ metallic glass J. of Non-Crys. Sol. 456 138–42

[22] Li X G, Ohtara T, Takahashi S, Shoji T, Kimura H M and Inoue A 2000 Hydrogen absorption and corresponding changes in structure and thermal stability of Zr$_{50}$Al$_{20}$Cu$_{10}$Ni$_{10}$Nb$_{5}$ amorphous alloy J. Alloys Comp. 297 303–11

[23] Jayalakshmi S, Kim K B and Fleury E 2006 Effect of hydrogen on the structural, thermal and mechanical properties of Zr$_{50}$–Ni$_{27}$–Nb$_{18}$–Co$_{5}$ amorphous alloy J. Alloys Comp. 417 195–202

[24] Hoedzel M, Danilkin S A, Ehrenberg H, Toebbens D M, Udovic T J, Fues H and Wipf H 2004 Effects of high-pressure hydrogen charging on the structure of austenitic stainless steels Mater. Sci. Eng. A 384 255–61

[25] Oliver W C and Pahr G M 1992 An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments J. Mater. Res. 7 1564

[26] Dong F, Lu S, Zhang Y, Luo L, Su Y, Wang B, Huang H, Xiang Q, Yuan X and Zuo X 2017 Effect of hydrogen addition on the mechanical properties of a bulk metallic glass J. of Alloys and Comp. 695 5183–90

[27] Dong FY, Su Y Q, Luo L S, Wang L, Wang SJ, Guo J J and Fu H Z 2012 Enhanced plasticity in Zr-based bulk metallic glasses by hydrogen Int. J. Hydrog. Energy 7 349 1697–701

[28] Dandana W and Hajlaoui K 2018 Effect of hydrogen addition on the mechanical properties of Zr-based metallic glass J. of Alloys and Comp. 742 563–6

[29] Dong F, He M, Zhang Y, Wang B, Luo L, Su Y, Yang H and Yuan X 2019 Investigation of shear transformation zone and ductility of Zr-based bulk metallic glass after plasma-assisted hydrogenation Mater. Sci. Eng. A 759 105–11

[30] Suh D and Daukardt R H 2000 Hydrogen effects on the mechanical behavior and fracture behavior of a Zr65.5Ni23Cu17 metallic glass Sci. Mater. 42 233

[31] Suh D, Asoka-Kumar P and Daukardt R H 2002 The effects of hydrogen on viscoelastic relaxation in Zr65.5Ni23Cu17 bulk metallic glasses: implications for hydrogen embrittlement Acta Mater. 50 537–51

[32] Shan G B, Li X, Yang Y Z, Qiao J L and Chu W Y 2007 Hydrogen enhanced plastic deformation during indentation for bulk metallic glass of Zr$_{52}$Al$_{15}$Ni$_{15}$Cu$_{18}$, Mater. Lett. 61 1625–8

[33] Kirchheim R, Sommer F and Schlückebier G 1982 Hydrogen in amorphous metals I Acta Metall. 30 1059–68

[34] Kirchheim R 1988 Hydrogen solubility and diffusivity in defective and amorphous metals Prog. Mater. Sci. 32 261–325

[35] Su Y Q et al 2012 Bulk metallic glass formation: the positive effect of hydrogen J. Non. Cryst. Solids 358 2606–11

[36] Flores K M, Sherer E, Bharathula A, Chen H and Jean Y C 2007 Subnanometer open volume regions in a bulk metallic glass investigated by positron annihilation Acta. Mater. 55 3403–11

[37] Zhao Y, Choi I C, Seok M Y, Ramamurti U, Suh J Y and Jang J I 2014 Hydrogen-induced hardening and softening of Ni–Nb–Zr amorphous alloys: dependence on the Zr content Seri. Mater. 93 56–9

[38] Dong F et al 2017 Effects of hydrogen on the nanomechanical properties of a bulk metallic glass during nanoindentation Inter. J. Hyd. Energy 42 25346–48

[39] Spaepen F 1977 A microscopic mechanism for steady state inhomogeneous flow in metallic glasses Acta Metall. 25 407–15
[40] Argon A S 1979 Plastic deformation in metallic glasses Acta Metall. 27 47–58
[41] Luo L S et al 2019 Structural origins for the generation of strength, ductility and toughness in bulk-metallic glasses using hydrogen microalloying Acta Mater. 171 216–30
[42] Zhao Y, Seok M Y, Choi I C, Lee Y H, Park S J, Ramamurty U, Suh J Y and Jang J I 2015 The role of hydrogen in hardening/softening steel: influence of the charging process Scripta Mater. 107 46–9
[43] Matsui H, Kimura H and Kimura A 1979 The effect of hydrogen on the mechanical properties of high purity iron III. The dependence of softening in specimen size and charging current density Mater. Sci. Eng. 60 227–34
[44] Barnoush A, Asgari M and Johnsen R 2012 Resolving the hydrogen effect on dislocation nucleation and mobility by electrochemical nanoindentation Scr. Mater. 66 414–7
[45] Kirchheim R 2012 Solid solution softening and hardening by mobile solute atoms with special focus on hydrogen Scr. Mater. 67 767–70
[46] Jayalakshmi S, Fleury E and Sordelet D J 2009 High temperature properties of hydrogenated Ti_{50}Zr_{25}Co_{25} rapidly quenched alloy J. Phys. Conf. Ser. 144 012120
[47] Yoo B G, Oh J H, Kim Y J and Jang J I 2010 Effect of hydrogen on subsurface deformation during indentation of a bulk metallic glass Intermetallics 18 1872–5