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Effect of hydrogen on subsurface deformation during indentation of a bulk metallic glass

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ABSTRACT

The influence of hydrogen on the plastic deformation of bulk metallic glasses (BMGs) was analyzed by recourse to nanoindentation of subsurface deformation produced during macroscopic indentation of the as-cast and hydrogen-charged samples. Results reveal that hydrogen restricts the plasticity (that is, shear band evolution) and thus significantly enhances hardness. The deformed regions of both the as-cast and hydrogen-charged samples exhibit plastic flow softening. This study demonstrates that the hydrogen affects the plastic deformation of BMGs in a manner that is similar to structural relaxation. This is due to the similar influence both of them have on reducing the free volume content.

1. Introduction

While bulk metallic glasses (BMGs) have been considered as potential hydrogen storage materials [1], understanding of the hydrogen effect in BMGs is far from complete compared to the considerable progress that has been achieved in crystalline materials.

There have been efforts to analyze the deformation behavior of hydrogen-introduced BMGs through conventional mechanical tests [2–4]. However, conventional tests (such as uniaxial tensile/compression and bending) have some limitations in clarifying the fundamental nature of the hydrogen effect in BMGs due to the very limited plasticity of hydrogen-introduced BMG materials. A way widely used to overcome this difficulty is the instrumented indentation test (IIT) which can provide sufficient information about elastic–plastic deformation of various BMGs during entire loading and unloading sequences [5].

In this study, we attempted to systematically investigate the influence of hydrogen on the macro- and micro-scale plastic deformation of a Zr-based BMG by performing both macroscopic indentation and nanoindentation. The results are discussed in terms of hydrogen-induced structural change, especially with regard to free volume.

2. Experiments

The examined materials are $(Zr_{52.5}Ni_{13.6}Cu_{18}Al_{10.4})Nb_2$ BMGs in both as-cast and hydrogen-charged states. Hydrogen was introduced into the sample by cathodic charging in a 1 N H_2SO_4 + 0.25 g/l As_2O_3 solution. The charging was made for 50 h and 100 h under a constant current density of 50 mA/cm^2. To investigate the possible structural changes due to hydrogen charging, X-ray diffraction (XRD) analysis was conducted using D/MAX-2500 (Rigaku-Denki, Japan).

The interface-bonded specimens for macro-scale spherical indentation were prepared according to the procedure introduced in [6–11]. On the bonded interface, spherical indentation was carried out using AIS2100 (Frontics Inc., Seoul, Korea) with an indenter having a radius of 500 μm. The maximum indentation load was 196 N, and the loading rate was fixed as 5 μms^{-1}. After macro-indentation, samples were detached and then the subsurface morphology was observed through optical microscopy. Subsequently, the deformed region was polished again into a flat surface using 0.3 μm alumina. On the gently polished region, a series of nanoindentations were performed using a Nanoindenter-XP (Nano Instruments Corp., Oak Ridge, TN) with a Berkovich indenter. The maximum indentation load and loading rate were fixed as 50 mN and 0.1 s^{-1}, respectively. Additionally, the profiles of nanoindentation morphology were analyzed by atomic force microscopy (AFM) XE-100 (Park System, Suwon, Korea).

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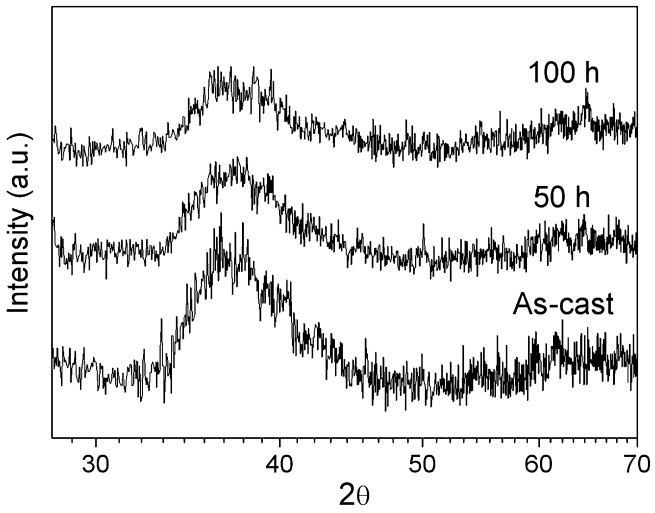

Fig. 1. XRD patterns of as-cast and hydrogen-charged specimens.

3. Results and discussion

Fig. 1 shows the XRD scans of the as-cast and charged samples. Because no crystalline peaks were detected in the XRD spectra of any sample, it was convinced that metal hydrides (that are often responsible for hydrogen embrittlement in Zr-containing crystalline alloys) were not formed in the charged samples.

The optical micrographs of the deformation region underneath the spherical impression are shown in Fig. 2. In the as-cast and charged samples, both the size of the subsurface deformation zone (where multiple shear bands are developed) and the shear band number density decrease with hydrogen charging time. In the as-cast sample [Fig. 2(a)], two different types of shear bands (i.e., semicircular and radial) are observed. In the charged samples [Fig. 2(b) and (c)], however, the secondary radial shear bands are rarely observed within the subsurface region. This implies that the hydrogen charging significantly reduced the shear band activities and thus limited the plasticity.

In order to analyze the mechanical response of the deformed region in Fig. 2, nanoindentation experiments were performed on the deformed area after gentle polishing. The representative load–displacement (P–h) curves obtained from undeformed and deformed regions are compared in Fig. 3. For both the as-cast and hydrogen-charged samples, the peak-load displacement of the deformed region is much larger than that of the undeformed region, which implies that the deformed region has lower hardness.

The nanoindentation hardness distribution within the region underneath macroscopic indentation impression is mapped in Fig. 4 with a background of optical microscopy image for the subsurface deformation morphology. Note that the nanoindentation hardness values were calculated according to the Oliver–Pharr method [12]. Since this method cannot take the pile-up (typically observed around the hardness impression of BMGs) into consideration, the hardness value reported here is an overestimate. In Fig. 4, it is obvious that the deformed region of both as-cast and charged sample was indeed softened [Fig. 4(b)] although there is some fluctuation in hardness value. Variation in the nanohardness value with hydrogen charging time is summarized in Fig. 5. It is clearly seen that, for both deformed and undeformed region, more charged sample exhibits higher hardness.

The detailed mechanism of hydrogen-induced hardening is not yet fully understood. Nevertheless, from the above results, one may gain a clue to explain it: The effects of hydrogen charging observed above are somewhat analogous to that of the structural relaxation by sub-T_g annealing [11]. Sub-T_g annealing of BMGs leads to free

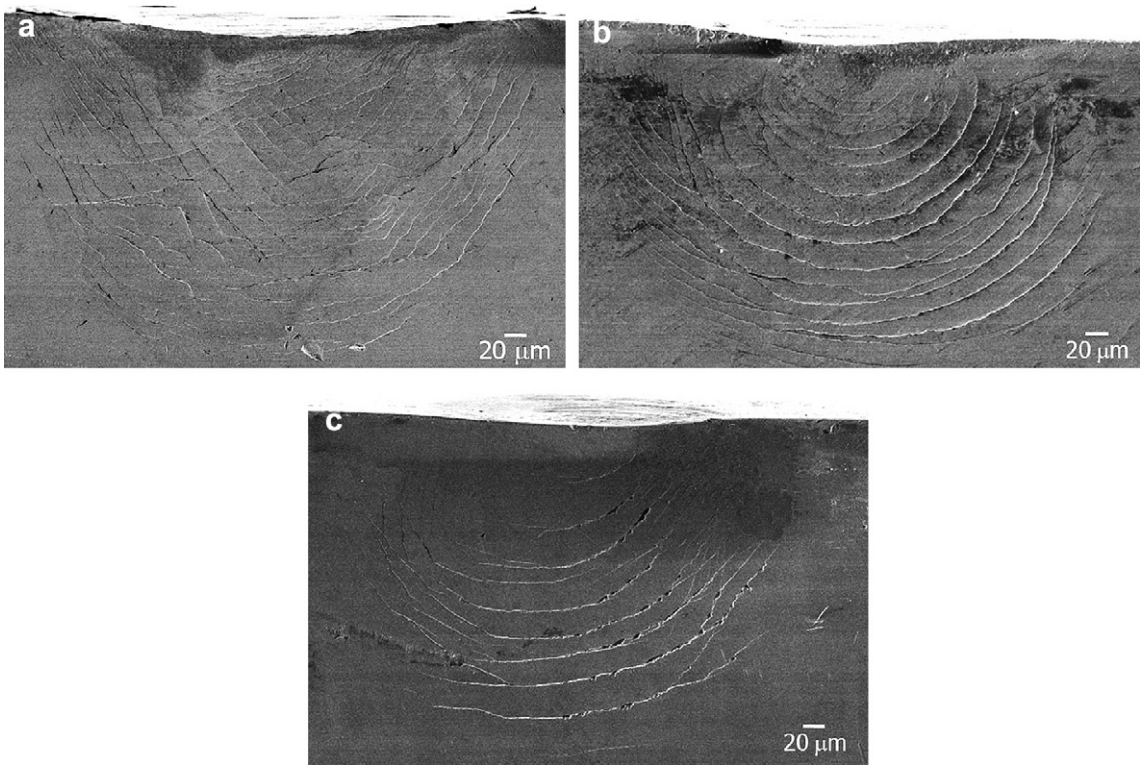

Fig. 2. Optical micrographs showing the development of subsurface deformation underneath the macroscopic spherical indentation made at $P_{max} = 196$ N; (a) as-cast, (b) 50 h-charged, and (c) 100 h-charged sample.

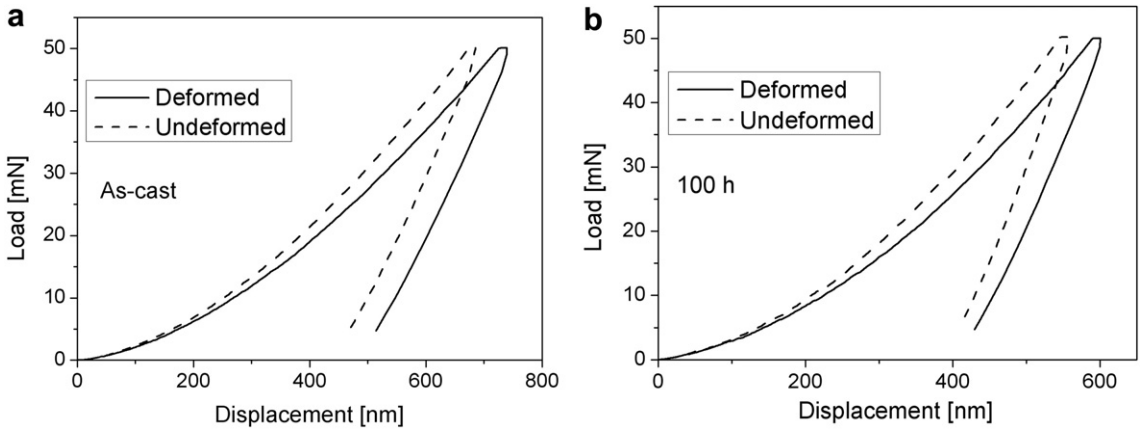

Fig. 3. Representative *P–h* curves obtained at the peak-load of 50 mN and constant strain rate of 0.1/s; (a) as-cast and (b) 100 h-charged sample.

volume reduction by annihilation, and thus the annealed sample generally exhibits much higher hardness than the as-cast one [11]. Based on the similarity of the plastic deformation between the annealed sample and the hydrogen-charged sample, one may imagine that the amount of free volume was significantly reduced by hydrogen charging. A hypothesis is possible based on the assumption that the free volume is a good site for trapping hydrogen atom that is the lightest element in the periodic table. Once open free volume is occupied by hydrogen atom, it cannot play a role in plastic deformation anymore. Thus, from the viewpoint of structural defect, the hydrogen-charged BMG can behave like a sub-T_g annealed BMG. Similarly, Suh and Dauskardt [13] suggested an indirect evidence of the free volume reduction in hydrogen-charged Zr-based BMG samples through DSC data analysis. An attempt to directly measure the change in free volume amount by hydrogen charging was made by Flores et al. [14]. Using positron annihilation spectroscopy, they demonstrated that the free volume surrounded by hydride-forming elements (Zr, Ti) could trap the hydrogen atoms, leading a smaller free volume after hydrogen trapping.

Another possibility for hydrogen-induced hardening behavior can be proposed in consideration of the hydrogen embrittlement mechanisms, because hardening and embrittlement can take place together (due to the competing nature of fracture and deformation). Among several mechanisms suggested for the hydrogen embrittlement in crystalline materials (such as the high-pressure bubble formation [15], the reduction of cohesion between interatomic bonds [16], hydride formation [17], and interaction with dislocations [18]), only the formation of strong metal hydride can be a cause of the hydrogen-induced hardening in BMG. However, this possibility can be ruled out in present work, because any peak of crystalline phase (including hydride) was not detected in XRD analysis of the tested samples. Collectively, the hardness increase and plasticity reduction by hydrogen charging might be attributed to the decrease in 'available' free volume that can contribute to the

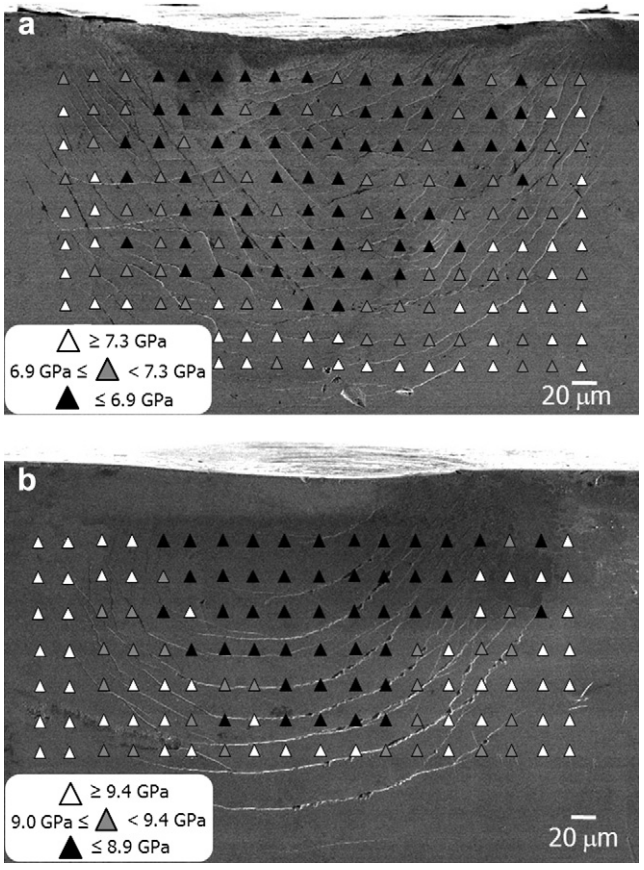

Fig. 4. Nanohardness distribution map in the subsurface deformation region; (a) as-cast and (b) 100 h-charged sample.

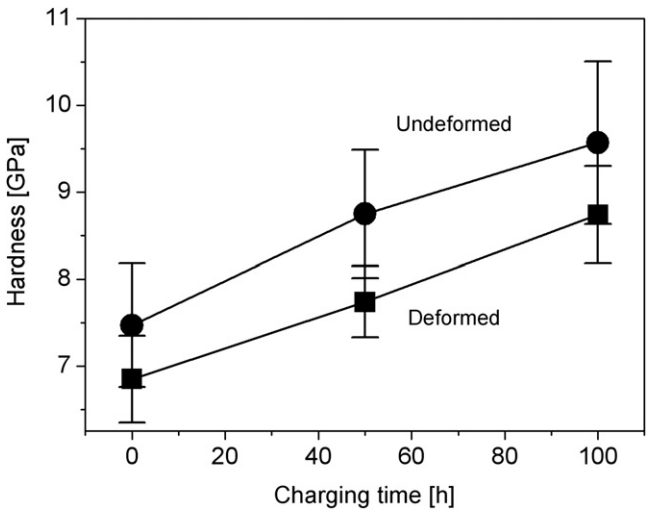

Fig. 5. Summary of the change in nanohardness as a function of hydrogen charging time.

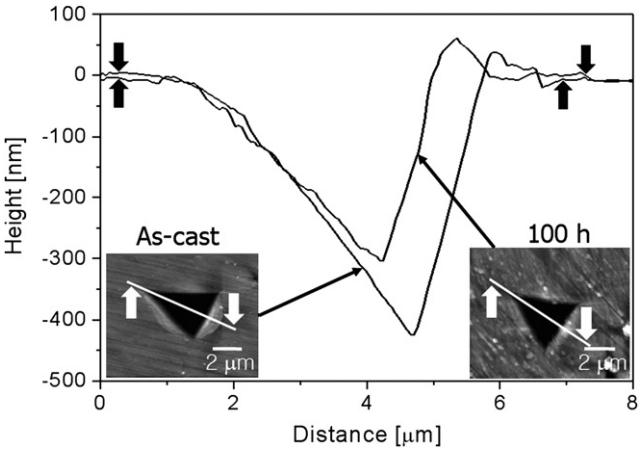

Fig. 6. Typical example of AFM analysis of the nanoindentation impression made in the undeformed region.

plastic deformation of the BMG. It is noteworthy that, as shown in Figs. 4 and 5, even the hydrogen-charged samples experienced the work softening possibly due to the creation of excess free volume during macroscopic indentation.

Surface profiles around the nanoindentation impressions of the as-cast and charged samples were examined using AFM. From the representative line-scan profile shown in Fig. 6, it is clearly seen that, while the final indentation depth for the as-cast sample is higher than that for the charged one, the material pile-up around the indentation is more significant in the charged sample than that in the as-cast one. This AFM result supports the free volume-based mechanism mentioned above; that is, since the charged specimens have a reduced ability to accommodate the deformation due to the reduction in free volume, more material (removed from indented volume) can pile-up around indentation.

4. Conclusion

Plastic deformation of the as-cast and hydrogen-charged BMGs was examined by using the instrumented indentation technique. While hydrogen charging enhanced the nanohardness, both the deformed zone size and shear band density decreased with charging time. Subsequent nanoindentation experiments revealed that the deformed region under the indenter was indeed softened. Interestingly, the subsurface deformation behavior of the hydrogen-charged samples was somewhat analogous to that of sub-T_g annealed samples, and thus hydrogen effects could be discussed in terms of free volume amount.

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