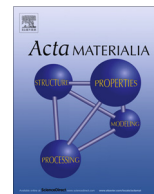




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Effectiveness of hydrogen microalloying in bulk metallic glass design

D. Granata, E. Fischer, J.F. Löffler*

Laboratory of Metal Physics and Technology, Department of Materials, ETH Zurich, 8093 Zurich, Switzerland

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ABSTRACT

We investigate the effect of hydrogen microalloying in Pd-based and Zr-based bulk metallic glasses (BMGs). To this end, we study the solubility and diffusivity of hydrogen in glassy $\text{Pd}_{77.5}\text{Si}_{16.5}\text{Cu}_6$ and $\text{Zr}_{64}\text{Cu}_{22}\text{Al}_{12}$, and focus on its beneficial effect on glass-forming ability and malleability. Each system reveals a different affinity with hydrogen and hence a different stability of hydrogen incorporation. In the case of the Pd-based BMG, large hydrogen pressures are required during processing and only small amounts of hydrogen can be incorporated into the glassy structure. This hydrogen, however, can rapidly diffuse out of the sample even at room temperature, with a calculated diffusion coefficient that agrees with literature results. In contrast, the Zr-based BMG features much greater hydrogen solubility and the incorporated hydrogen is strongly bonded to Zr. Thus hydrogen microalloying is found to have a beneficial long-term effect on BMG malleability only for systems where sufficient amounts of incorporated hydrogen can bond strongly to the base element. We also discuss the implications of these findings for future BMG design.

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1. Introduction

From an engineering and application-oriented perspective, enhancing the limited room-temperature plasticity of bulk metallic glasses (BMGs) [1–3] appears to be a key challenge. However, improving the understanding of the factors which determine the malleability of a particular composition is crucial if we are to design ductile BMGs [4]. Approaches based on the introduction of either porosity [5,6], crystalline reinforcing phases [7,8], or soft graphite particles [9] substantially enhance the attainable ductility. These routes, however, often adversely affect beneficial properties of BMGs such as high fracture strength and improved corrosion resistance [4]. In the case of monolithic BMGs, plasticity is mainly affected by the specific alloy chemistry and processing parameters such as cooling rate [10,11]. In most glass-forming systems malleability can therefore be fine-tuned by proper alloying, as the degree of structural short-range order is greatly composition-dependent [12]. In this light, alloy design centered on microalloying, i.e., minor additions of suitable alloying elements, appears to be a promising approach for enhancing BMG ductility [13,14].

Recently, minor doping with hydrogen has been found to simultaneously improve the glass-forming ability (GFA) and the compressive ductility of Zr-based BMGs [15–17]. Such

processing-induced microalloying incorporates hydrogen directly into the glassy structure, resulting in a higher packing density, as illustrated by positron annihilation spectroscopy (PAS) [15], and increased local inhomogeneity [16]. This increased structural heterogeneity is thought to promote the multiplication of shear bands and accordingly enhance the attainable ductility [18]. However, the durability of the hydrogen-induced beneficial effects must be studied in greater detail because of the common incidence of high hydrogen diffusivity. In this paper we therefore investigate how hydrogen microalloying affects the plasticity of $\text{Pd}_{77.5}\text{Si}_{16.5}\text{Cu}_6$ [19,20] and Zr-rich $\text{Zr}_{64}\text{Cu}_{22}\text{Al}_{12}$ [16,21] BMGs. In this context we first investigate the solubility and diffusivity of hydrogen in both systems. In the case of the Pd-based BMG the small amount of incorporated hydrogen reduces greatly with room-temperature aging and, based on this time-dependent hydrogen out-diffusion, a corresponding hydrogen diffusion coefficient can be calculated. The Zr-based BMG, in contrast, exhibits much higher hydrogen solubility and strong hydrogen bonding to Zr, which generates a constant hydrogen concentration over time. We discuss in detail the efficacy of hydrogen microalloying and show that long-term enhancement of BMG malleability can only be maintained for systems where a sufficient amount of incorporated hydrogen can strongly bond to the base element. Based on these results we also discuss implications for future BMG design and suggest further promising glass-forming systems to which hydrogen microalloying could be beneficially applied.

* Corresponding author.

E-mail address: joerg.loeffler@mat.ethz.ch (J.F. Löffler).

2. Experimental procedure

All master alloys were prepared by melting high-purity metals in an arc melter (Edmund Bühler GmbH) under inert-gas atmosphere. Amorphous 2 mm Pd_{77.5}Si_{16.5}Cu₆ and 3 mm Zr₆₄Cu₂₂Al₁₂ (Zr64) rods were then produced by suction casting into water-cooled Cu molds. In the case of hydrogen-microalloyed specimens, alloying and casting was performed under a mixture of 95% Ar and 5% hydrogen (6 N purity). The Pd-based glasses were produced with an applied overpressure of 800 mbar, whereas the Zr-based specimens were produced at an overpressure of 100 mbar. In the following these alloys are denoted as H₂-alloyed Pd–Si–Cu and H₂-alloyed Zr64 BMGs. In order to determine the effect of hydrogen, Pd_{77.5}Si_{16.5}Cu₆ and Zr₆₄Cu₂₂Al₁₂ BMGs were also alloyed and cast as reference alloys under pure Ar atmosphere (6 N purity) and denoted as Ar-cast Pd–Si–Cu and Ar-cast Zr64. The microstructure of all specimens was investigated via X-ray diffraction (XRD) using a Stoe STADI X-ray diffractometer in Bragg–Brentano geometry, with a fixed incoming angle of 20° and a 140° image plate detector (Stoe, IP-PSD). Monochromatic Cu-K α ($\lambda = 0.15406$ nm) radiation was employed for all measurements. In the case of the H₂-alloyed Pd–Si–Cu samples the XRD measurements were performed as a function of time elapsed since sample preparation, to investigate time-dependent structural changes during hydrogen out-diffusion. The thermal properties were investigated using a Netzsch DSC 404 C Pegasus at a heating rate of 20 K per min.

The hydrogen concentrations were measured by means of inert-gas analysis (LECO ONH 836, LECO, St. Joseph, MI). Here the hydrogen present in the sample is oxidized to water, which is then detected using non-dispersive infra-red cells. Calibration was performed using different hydrogen standards (LECO, St. Joseph, MI) and masses larger than 200 mg, which is in line with the mass sensitivity of the method employed. Because the hydrogen is more strongly bonded in the Zr–Cu–Al alloys, Ni baskets and tin capsules were utilized as fluxing agents to precisely analyze the incorporated hydrogen. The prepared rods of 3 cm in length and 2 mm and 3 mm in diameter were sectioned into 7 specimens of equal length ($l \approx 4$ mm) and hence of nearly equal mass. For time-dependent measurements, the hydrogen concentration was determined by averaging the values obtained along the rod.

Compression tests were performed using a screw-driven Schenck-Trebel compression machine at a strain rate of $2 \times 10^{-3} \text{ s}^{-1}$. For this purpose the rods were cut into specimens with a fixed length-to-diameter aspect ratio of 2:1 and polished plane-parallel to exclude any geometrical constraint on the attainable ductility. Accordingly, the geometry of the tested rods was 2 mm diameter by 4 mm length for Pd–Si–Cu and 3 mm diameter by 6 mm length for Zr–Cu–Al.

3. Results and discussion

The glassy nature of all Ar-cast and H₂-alloyed samples was confirmed by means of XRD and DSC. Fig. 1a presents the XRD patterns of the Ar-cast and H₂-alloyed Pd–Si–Cu rods of 2 mm diameter, which both appear to be amorphous. This finding is comprehensible because the diameter of the specimens prepared is slightly lower than the reported critical casting thickness [22]. Similarly, Fig. 1b depicts the XRD patterns of Ar-cast and H₂-alloyed Zr64 samples of 3 mm diameter. Both modifications are also found to be amorphous in this case, because their respective XRD patterns only feature halos characteristic of the glassy state. The halo of Ar-cast Zr64, however, appears sharper than that of the hydrogen-processed counterpart, which is in line with the finding that hydrogen microalloying generates enhanced GFA [15–17].

Fig. 2 presents differential scanning calorimetry (DSC) scans of Ar-cast and H₂-alloyed Pd–Si–Cu and Zr64. All scans exhibit an endothermic signal associated with the glass transition T_g and two exothermic crystallization peaks (T_{x1} and T_{x2}), indicating a two-step crystallization process in the amorphous samples [23]. In both alloy systems hydrogen microalloying is found to only slightly change the values of T_g , the onset of crystallization T_{x1} , and the supercooled liquid range ΔT , as is shown in Table 1. However, it appears to strongly affect the crystallization behavior of Zr64 alloys, which is evident in a decreased second crystallization temperature T_{x2} and modified peak shapes pointing to different crystallization kinetics. Recent results on the crystallization of thin Zr–Cu–Al metallic glass films [24] indicate that the main factor affecting the nucleation rate in these alloys is the mobility of the base metal Zr. Alloying with Al results in a decreased Zr diffusivity due to the formation of strong Zr–Al bonds suppressing the nucleation of primary Zr- and Al-rich phases, hence generating improved crystallization resistance [24]. As the mixing enthalpy of the Zr–H bonding pair (-69 kJ/mol [25]) is even more negative than that of Zr–Al (-44 kJ/mol [25]), the mobility of Al may increase again due to the preferred formation of strong Zr–H bonds. This apparently affects the kinetics of the secondary crystallization process via the nucleation of competing phases with greater Al and Cu contents, as is indeed experimentally observed.

To investigate the efficacy of hydrogen microalloying in more detail, the solubility and diffusivity of hydrogen was examined in both Pd–Si–Cu and Zr64 BMGs. The hydrogen content was measured by means of inert-gas analysis and determined as a function of rod length. Fig. 3a presents the hydrogen concentration along the rod for H₂-alloyed and Ar-cast Pd–Si–Cu BMGs directly after preparation. Processing under hydrogen-containing atmosphere enhances the amount of incorporated hydrogen by a factor greater than 8. The average hydrogen concentrations of H₂-alloyed and Ar-cast Pd–Si–Cu BMGs are 12.9 wt.ppm and 1.5 wt.ppm, respectively (corresponding to 0.12 at.% for H₂-alloyed and 135 at.ppm for Ar-cast Pd–Si–Cu). The small amount of hydrogen measured in the Ar-cast alloys presumably originates from impurities present in the raw materials and/or some contamination during the casting process. This agrees with Ref. [26], which reports that the hydrogen content of untreated Pd-based alloys already exceeds 100 at.ppm. Despite the high hydrogen affinity of the base metal Pd, only small amounts of hydrogen can be dissolved in H₂-alloyed Pd–Si–Cu BMGs. This agrees with Ref. [27], where it was found that Pd–Si-based amorphous alloys absorb only low amounts of hydrogen at pressures below 10 MPa. However, greater hydrogen concentrations may be achieved by applying higher hydrogen overpressures during sample preparation, in line with Sievert's law [28].

The situation looks quite different for the Zr-based glasses, where large hydrogen concentrations can be attained even at low applied hydrogen pressure. Fig. 3b illustrates the hydrogen content measured along H₂-alloyed and Ar-cast Zr64 rods. Via processing in hydrogen-containing atmosphere, the hydrogen concentration within the sample can be enhanced by a factor of around 11. Accordingly, the average hydrogen concentrations measured by inert-gas analysis are 200.3 wt.ppm (1.5 at.%) for H₂-alloyed and 18.3 wt.ppm (0.14 at.%) for Ar-cast Zr64 BMGs, respectively. The Zr64 BMGs show a much higher affinity to hydrogen than Pd-based glasses, and Ar-cast Zr64 already features a greater hydrogen content than the H₂-alloyed Pd-based glass. The hydrogen incorporation is significantly more effective in Zr64, which is also supported by the fact that the Zr64 BMGs were prepared at a low applied casting pressure of 100 mbar, whereas an overpressure of 800 mbar was applied in the case of H₂-alloyed Pd–Si–Cu. Casting of the Zr64 BMG at a similarly high overpressure yielded a hydrogen concentration of around 285 wt.ppm, in line with earlier results [16].

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