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Absorption/desorption behavior of hydrogen and deuterium in a Pd-coated Zr-based amorphous alloy

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Abstract

Palladium (Pd) coating was found to enhance significantly the absorption/desorption behavior of hydrogen in amorphous $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$, thereby improving the applicability of this alloy to hydrogen storage systems. This paper demonstrates the different characteristics of deuterium/hydrogen absorption/desorption in this Pd-coated metallic glass. Pd-coated amorphous ribbons were electrochemically charged with hydrogen or deuterium to various concentrations. Absorption and desorption characteristics were determined by means of a hydrogen determinator and thermal desorption spectroscopy (TDS), respectively. Hydrogen effects on the thermal stability and crystallization characteristics were studied using differential scanning calorimetry (DSC), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The hydrogen uptake was found to be twice faster than that of deuterium. Hydrogen-induced phase transformations, however, might prevent the use of this alloy for hydrogen storage applications.

Keywords: Amorphous alloys; Hydrogen storage; Hydrogen isotopes; Thermal desorption spectroscopy (TDS); Zr-based alloys

1. Introduction

Zr–Cu–Ni–Al metallic glasses are among the best glass-forming alloys known. Their high thermal stability is related to a wide undercooled liquid region, which precedes crystallization into multiple intermetallic phases [1]. These materials also exhibit favorable hydrogen–metal chemistry, being composed of early and late transition metals, as well as local tetrahedral short-range order, which makes them candidates for hydrogen storage applications. In previous studies [2–4] it was reported that amorphous Zr–Cu–Al–Ni alloys can absorb significant contents of hydrogen (up to about 1.0 H/M), comparable with several materials for hydrogen storage applications such as crystalline $LaNi_5$ and TiFe alloys. Unfortunately, a very thin layer of ZrO_2 (several nanometers in thickness), formed during or just after electrochemical charging, prevented the full recovery of hydrogen even at temperatures as high as 700 °C [4]. Oxide layers are considered to not only hinder hydrogen diffusivity, but also reduce the dissociate chemisorption of hydrogen on surfaces. Thus, it became essential to develop methodologies for surface activation and/or removal of surface barriers.

One possible concept to overcome the problem of surface barriers is to deposit Pd on the surface of the alloy. Pd does not oxidize and allows rapid hydrogen diffusion both through its outer surface and through its bulk. Thus, melt-spun $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ ribbons were vapor deposited in this work with a thin layer (~ 100 nm) of Pd. The following sections describe in detail the methodology, the effect of hydrogen on the thermal stability of the Pd-coated amorphous alloy, and the

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characteristics of hydrogen and deuterium absorption and evolution in this alloy.

2. Experimental

The pre-alloys were prepared by melting Zr, Cu, Ni and Al in an arc furnace under argon atmosphere (~ 1.2 bar) on a water-cooled copper substrate. From these pre-alloys amorphous ribbons (2 mm wide, 40 μm thick) with the nominal composition of $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ were prepared by melt spinning in a He atmosphere of 300 mbar. The temperature of melt was between 1100 and 1300 °C before casting. Then, the amorphous ribbons were coated with a 100 nm layer of palladium by vapor deposition. Pd-coating exhibited sufficient adhesion to the amorphous ribbons. Hydrogen and deuterium charging were carried out electrochemically in a 2:1 (by volume) glycerine:phosphoric acid electrolyte and a 2:1 glycerine:d_3-phosphoric acid (D_3PO_4), respectively, at room temperature and a current density of 5 A m^{-2} for different charging times.

The total content of hydrogen and deuterium absorbed in the alloy, as well as the residual hydrogen content following differential scanning calorimetry (DSC) or thermal desorption spectroscopy (TDS) experiments, was measured by a LECO RH-404 hydrogen determinator system. The test protocol used was as follows. Following system calibration, the ribbons were placed inside a tin capsule, weighted, and then dropped into a graphite crucible. A high power electrode furnace (EF-500) subsequently passed high current through the crucible. The hydrogen released from the fused sample was swept (with other desorbed gases) by argon carrier gas through a series of filters to a molecular sieve column. After hydrogen was separated from the other gases, it was quantified in a sensitive thermal conductivity cell. The RH-404 determinator has an accuracy of ±0.05 ppm (or 2% of the reading, whichever is higher).

Deuterium evolution was studied by TDS, a technique that involves measurement of the desorption rate of gas atoms, solute or trapped in the material, while heating the sample at a known rate. This measurement allows for accurate evaluation of the total quantity of atoms, desorbed within the temperature range of the experiment. The Pd-coated $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ amorphous specimens were electrochemically charged with deuterium for TDS experiments in order to reduce the background noise. After ultrasonic cleaning in ethanol, the specimen was placed in the specimen holder, the system was sealed and pumped down to 10 μPa. The heating rate (ramp) was 5–10 K min^{-1}, and the temperature range was 50–600 °C, both parameters being programmed into a temperature controller. While heating, the mass spectrometer was placed in a continuous mode for scanning atomic masses in the range of 3.5–4.5 amu. Quantification of several trapping parameters was carried out following the procedure described elsewhere [4].

The microstructure following desorption was studied using a Rigaku Type 2000 X-ray powder diffractometer and a Ni-filtered Cu-K_α radiation. Hydrogen effect on the thermal stability was investigated by means of DSC (Pyris-I from Perkin Elmer) in Ar atmosphere at a constant heating rate of 20 K min^{-1}.

Auger electron spectroscopy (AES) was used to study the chemical composition at the surface of the Pd-coated samples before and after hydrogen/deuterium charging. A PHI 549 SAM/AES/XPS system was used. The samples were mounted in a test chamber and a vacuum of ~0.1 μPa was drawn. Depth profiles were obtained using argon ion sputtering at working conditions (P ~ 13.3 μPa, V = 3 kV) which yielded a surface removal rate of ~20 Å min^{-1}. Quantitative analysis was based on tables of experimental atomic sensitivity factors [5].

3. Results and discussion

3.1. Absorption behavior

The amount of deuterium absorbed in the Pd-coated $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ amorphous alloy was measured by means of LECO analysis following electrochemical charging. The absorption behavior of deuterium was evaluated from plots of the deuterium-to-metal (D/M) ratio versus charging time (Fig. 1). When compared with the results we previously reported for hydrogen absorption in this Pd-coated amorphous alloy [6], it is evident that the kinetics of hydrogen absorption is about twice faster than that of deuterium. The idea of isotope-dependent absorption kinetics reminds the isotope dependence of hydrogen diffusion in crystalline metals.

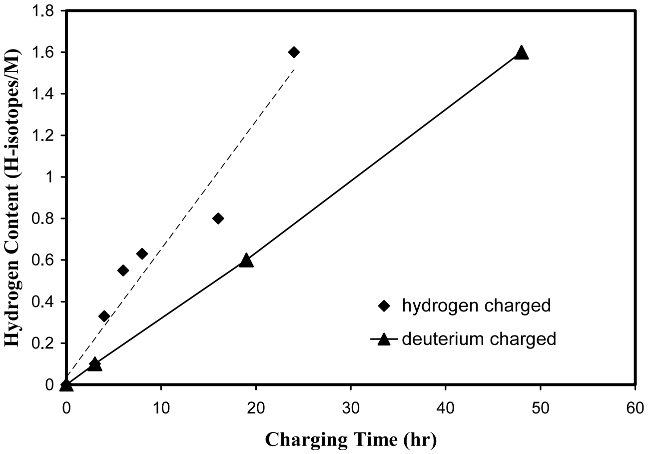

Fig. 1. Hydrogen and deuterium absorption in a Pd-coated $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ amorphous alloy, as measured by LECO hydrogen determinator following electrochemical charging at i = 5 A m^{-2}.

In *fcc* metals, for example, this dependence is nearly classical ($D_0 \propto m^{-1/2}$ and $E_a \propto m^0$) [7].

3.2. Desorption behavior

Deuterium evolution from the Pd-coated samples was studied in detail by TDS, applying heating rates (φ) from 3 to 10 K min^{-1}. Fig. 2 shows the TDS spectra of three samples pre-charged to different contents of deuterium (φ = 5 K min^{-1}). Obviously, as the sample is pre-charged with a higher content of deuterium, the intensity of desorption peaks increases. Consequently, the total amount of deuterium desorbed from the sample within that temperature range (i.e. the integral of desorption rate on time) increases too. Two desorption peaks (at 425 and 557 °C, respectively) are observed for the sample pre-charged to 0.1 D/M. However, when the material is pre-loaded with 0.6 D/M, four peaks are observed (at 253, 402, 501 and 560 °C, respectively). Four peaks (at 225, 332, 410 and 532 °C, respectively) are also observed for the material pre-loaded with 1.6 H/M. Thus, it can be concluded that as the Pd-coated amorphous alloy is charged with higher concentrations of hydrogen, the desorption peaks in the TDS spectra are both shifted to lower temperatures and increase in number. In order to confirm whether all deuterium was desorbed from the coated alloy within the temperature range of room temperature to 600 °C associated with the TDS experiments, LECO analyzes were carried out on these samples as well. Table 1 compares the amount of desorbed deuterium as obtained from TDS experiments to the amount of absorbed and residual deuterium as obtained from LECO analyzes before and after TDS experiments, respectively. It is evident that when the alloy is charged with low concentrations of deuterium (i.e. short charging time periods), almost all of the absorbed deuterium is desorbed during TDS experiments. However, as the alloy is pre-loaded with higher concentrations of deuterium, the concentration of the residual deuterium (i.e. deuterium that cannot be recovered during TDS) significantly increases too. This could be related to the occupation of deeper irreversible traps in the amorphous structure as well as to the formation of stable deuterium–metal compounds during charging with higher concentrations of deuterium. Comparing our TDS results to those reported on the uncoated alloy [4], the amount of deuterium desorbed from the Pd-coated alloy is higher by at least an order of magnitude, emphasizing the contribution of the Pd-coating to the improved absorption/desorption behavior of both hydrogen and deuterium in the $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ amorphous alloy. The shift of desorption peaks to lower temperatures with the increase in hydrogen content in the TDS spectra of the Pd-coated alloy is similar to the trend observed for the uncoated material [4].

Table 1
Amount of absorbed (LECO), desorbed (TDS), and residual (LECO) deuterium in a Pd-coated $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ amorphous alloy

Absorbed hydrogen (H/M)	Desorbed hydrogen (H/M)	Residual hydrogen (H/M)
1.00×10^{-1}	9.57×10^{-2}	4.00×10^{-3}
6.00×10^{-1}	5.76×10^{-1}	1.45×10^{-1}
1.6×10^{0}	1.4×10^{0}	2.20×10^{-1}

Deuterium charging was performed electrochemically at i = 5 A m^{-2}. TDS was carried out from room temperature to 600 °C at φ = 5 °C min^{-1}.

The influence of heating rate on the characteristics of deuterium desorption from Pd-coated amorphous specimens was studied too within the range of 3–10 K min^{-1}. Fig. 3 shows typical results for specimens pre-

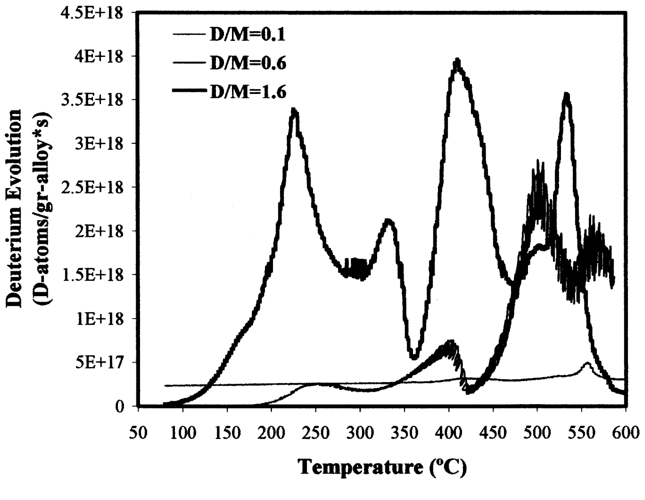

Fig. 2. TDS spectra showing deuterium evolution from Pd-coated samples pre-charged electrochemically at i = 5 A m^{-2} for different periods of time. φ = 5 °C min^{-1}.

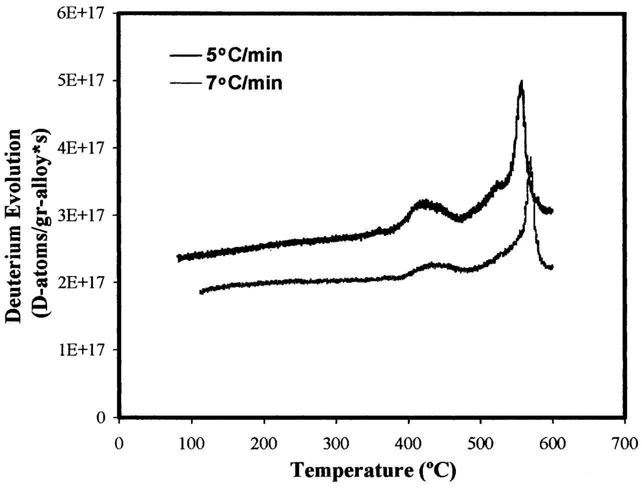

Fig. 3. Heating rate dependence of deuterium evolution from Pd-coated samples pre-charged electrochemically at i = 5 A m^{-2} to H/M = 0.1.

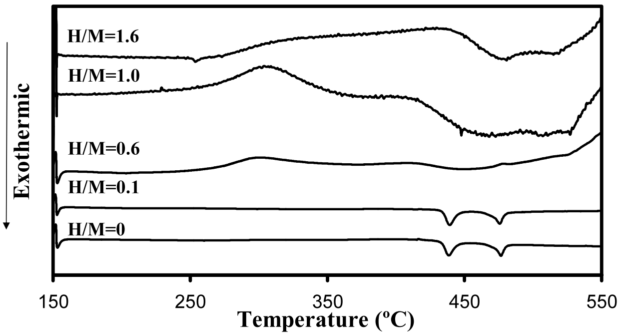

Fig. 4. DSC plots of uncharged and hydrogen charged Pd-coated amorphous samples. φ = 20 °C min^{-1} [6].

charged to D/M = 0.1 at i = 5 A m^{-2}. With increasing heating rates, the desorption peaks are shifted to higher temperatures and their intensities decrease (i.e. less deuterium is recovered).

The effect of hydrogen on the thermal stability of Pd-coated $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ amorphous alloy has already been reported in detail elsewhere [6]. Fig. 4 shows the DSC plots of the uncharged as well as hydrogenated alloy. In the case of hydrogenated specimens, endothermic peaks are evident in the DSC plots. Such endothermic peaks are often attributed to hydrogen desorption from hydrogenated amorphous alloys [8]. To prove this hypothesis, LECO analyzes were carried out immediately after terminating the DSC run (φ = 20 K min^{-1}) at the end of each endothermic or exothermic reaction. The results are shown in Fig. 5. This figure clearly illustrates the decrease in residual hydrogen content as heating is carried out. Yet, as seen in Fig. 5b, at high hydrogen contents (H/M = 1.6), more than 30% of the total amount of absorbed hydrogen remains in the alloy at the end of all phase transformations.

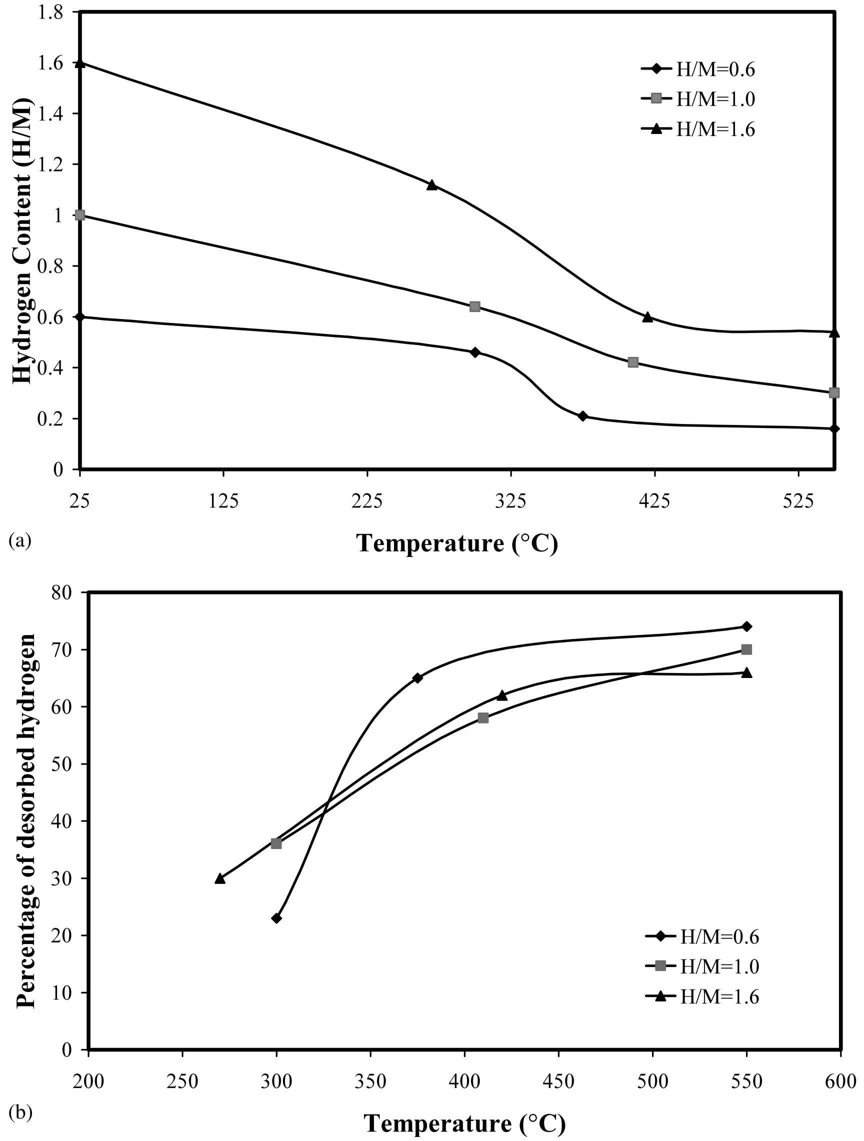

Fig. 5. Concentration of residual hydrogen (a) and percent of desorbed hydrogen (b) in hydrogen charged Pd-coated amorphous ribbons. Measurements were carried out by a LECO hydrogen determinator following DSC runs (φ = 20 °C min^{-1}) to various temperatures.

Microstructural investigations, by means of X-ray diffraction (XRD), of hydrogenated amorphous specimens that had been experimented in DSC revealed that complete desorption is obtainable only for low hydrogen contents (H/M < 0.35) [6]. At higher hydrogen contents (H/M > 0.6), an irreversible process of zirconium hydride (ε-ZrH_{2-x} and δ-ZrH_2) formation takes place and prevents the recovery of the original microstructure following (partial) hydrogen desorption [6].

3.3. Oxides formation

AES was used to determine the composition at, and just beneath, the surface of Pd-coated amorphous samples. AES depth profiles of uncharged as well as hydrogen charged samples are shown in Fig. 6. From this figure it is evident that the outer surface of the uncharged coated material consists of Pd as well as a very small atomic fraction of oxygen. The atomic fraction of Pd decreases with increasing sputtering time, as expected from a coating layer. In the case of electrochemically charged samples, Zr and O are observed at the outer surface. This oxide layer increases during the further uptake of hydrogen charging.

Figs. 7 and 8 present the AES depth profiles of uncoated and Pd-coated amorphous specimens, either uncharged or deuterium charged (24 h, H/M $\cong 0.6$). The calculated thickness of zirconium oxide layer on the uncoated material after deuterium charging was found to be equal to a few nanometers. The AES depth profiles of deuterium charged samples are almost identical to those of hydrogen charged samples. Comparing between the AES depth profiles of the uncoated deuterium charged specimen to the equally deuterium charged Pd-coated alloy, the uncoated surface is strongly saturated with oxygen, though the oxide layer is relatively thin, while, on the other hand, the oxygen presence in the Pd-coated surface is quite small. Obviously, Pd-

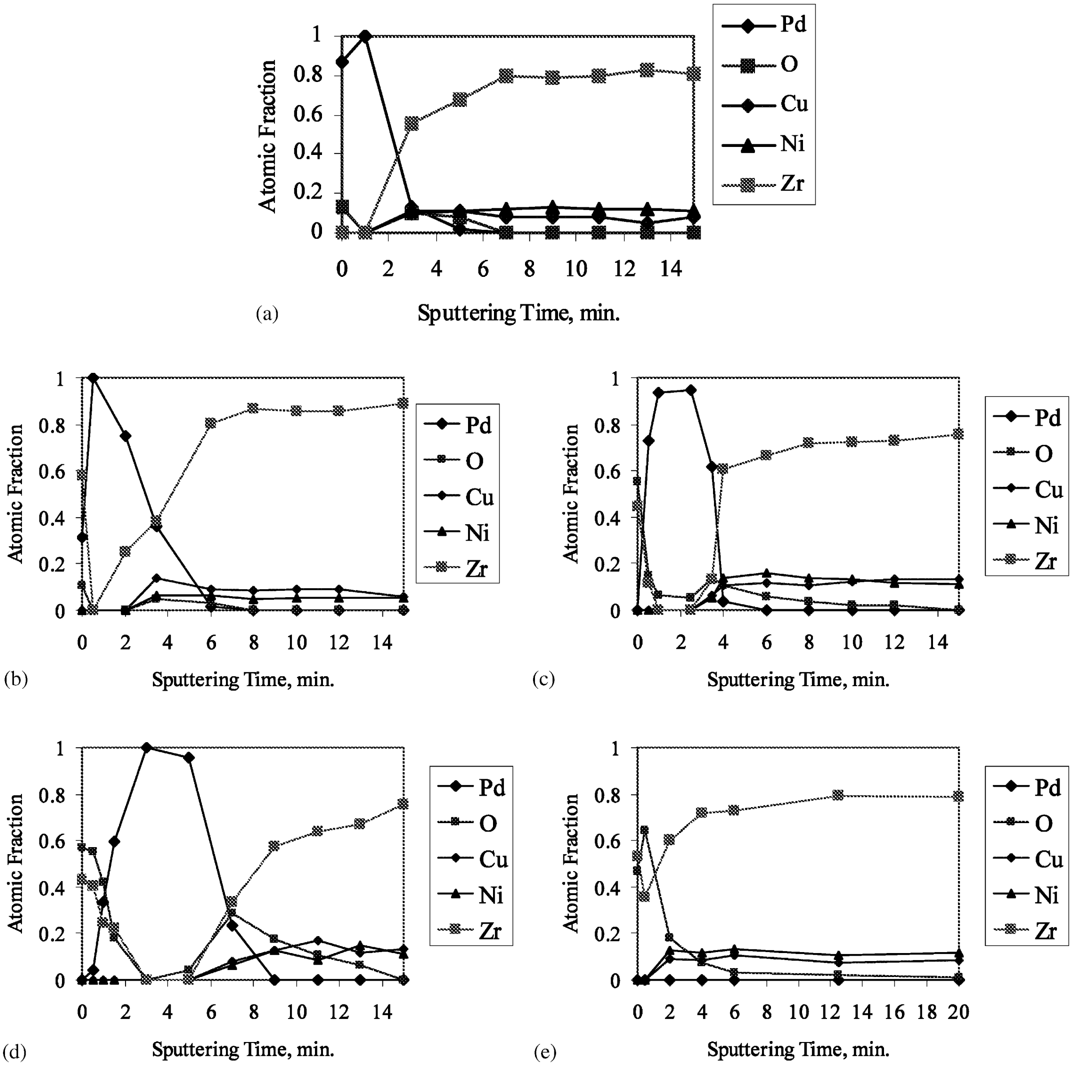

Fig. 6. AES depth profiles for uncharged (a) as well as hydrogenated (b–e) Pd-coated ribbons. Hydrogenation was carried out electrochemically at $i = 5$ A m^{-2} for different periods of time, yielding H/M $= 0.1$ (b), H/M $= 0.3$ (c), H/M $= 0.6$ (d) and H/M $= 1.6$ (e).

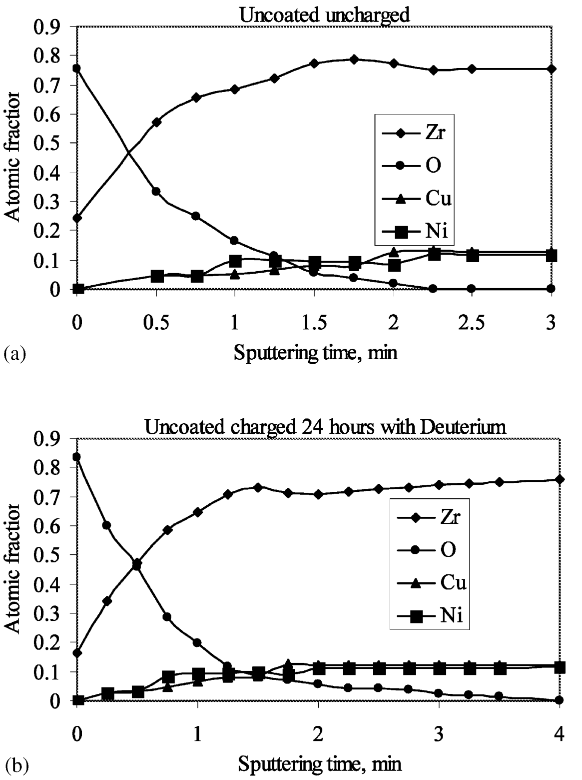

Fig. 7. AES depth profiles for (a) uncharged and (b) deuterium charged amorphous $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ alloy. Deuterium charging was carried out electrochemically at $i = 5$ A m^{-2} for 24 h.

coating prevents the formation of this oxide barrier in the surface and allows hydrogen/deuterium desorption in a relatively low temperature range (150–400 °C), in contrast to the uncoated metallic glass.

The TDS results shall now be interpreted in light of the DSC and LECO data. First, TDS spectra reveal (Fig. 2) that deuterium desorption from the Pd-coated samples starts at temperatures much below the onset temperature of ~ 350 °C reported for the uncoated amorphous alloy [4]. For example, desorption from the material pre-charged to $D/M = 1.6$ starts at a temperature of approximately 75 °C. In addition, as the Pd-coated amorphous alloy is charged with higher concentrations of deuterium, the desorption peaks are shifted to lower temperatures (see Fig. 2). We previously reported [2] that low hydrogen concentrations ($H/M < 0.15$) increase the thermal stability of the amorphous phase significantly. On the other hand, it was recently reported [6] that at high hydrogen concentrations ($H/M \geq 0.6$), ε-ZrH_{2-x} and δ-ZrH_2 are formed. Thus, phase transformations become more complex and start at lower temperatures as the concentration of hydrogen increases. Through comparison of the TDS data (Fig. 2) to the DSC data (Fig. 4), one may conclude that the high-temperature desorption peaks (above 430 °C) of alloys pre-charged with high contents of hydrogen are likely to be related to desorption that occurred during phase transformations.

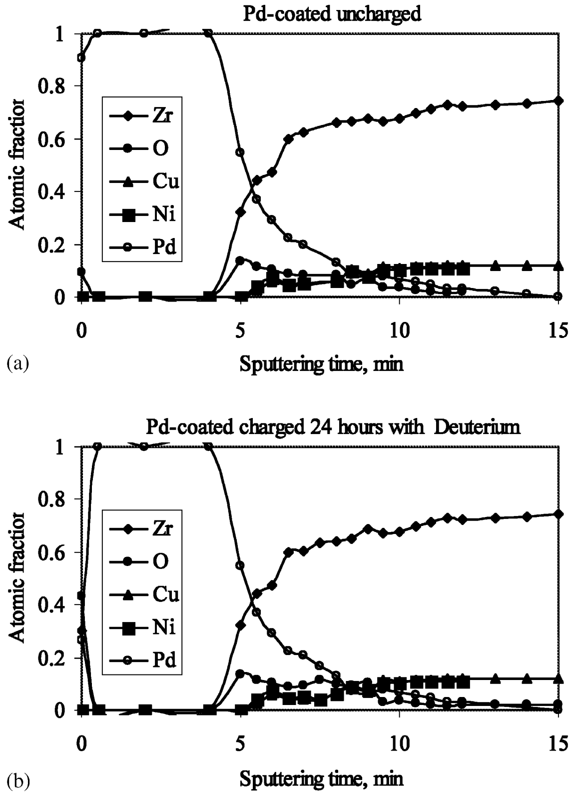

Fig. 8. AES depth profiles for (a) uncharged and (b) deuterium charged Pd-coated amorphous $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ alloy. Deuterium charging was carried out electrochemically at $i = 5$ A m^{-2} for 24 h.

4. Conclusions

Based on the results obtained in this work, the following conclusions may be drawn.

(i) Pd-coated $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ amorphous alloy can be charged electrochemically with a hydrogen content of 1.6 H/M, and even more. This hydrogen content is fairly high in comparison to various crystalline alloys often used to store hydrogen.

(ii) Pd coating improves significantly the absorption/desorption behavior of hydrogen and deuterium in amorphous $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ alloys. For example, it lowers the desorption onset temperature from above 350 °C to as low as 75 °C. In addition, it prevents the formation of surface barriers (oxides), that enables hydrogen/deuterium desorption, in contrast to the uncoated metallic glass.

(iii) In addition to hydrogen detrapping prior phase transformations, hydrogen release may also involve hydrogen desorption during phase transformations, such as the transformation of the amorphous matrix to the icosahedral phase and quasicrystals decomposition to different crystalline phases, or, at high hydrogen contents, the precipitation of different types of Zr-hydrides.

(iv) Similar to the isotope dependence of hydrogen diffusion in crystalline materials, the kinetics of hydrogen absorption in the Pd-coated metallic glass was found to be twice faster than that of deuterium.

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