

# Comparative study of deuterium desorption from Pd-coated Zr-based amorphous and quasicrystalline alloys

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## Abstract

Deuterium absorption in and desorption from Pd-coated amorphous and partially quasicrystalline  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  alloys were studied, using LECO, thermal desorption spectroscopy and X-ray diffraction. Desorption was affected by different trapping sites and phase transformations, and began earlier from the amorphous material. Palladium coating significantly enhanced the absorption/desorption behavior. Suitable heating rates for recovery were identified.

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## 1. Introduction

Amorphous and quasicrystalline alloys have been shown to possess structural characteristics and properties markedly different from their crystalline counterparts. While amorphous materials have already gained a wide variety of technological applications, only a few of the many applications foreseen following the discovery of quasicrystals by Shechtman et al. [1] have indeed been commercialized [2].

The storage capacity of hydrogen in metals and alloys is determined by chemical interactions between the metal and hydrogen atoms, as well as by the type, size and number of potential interstitial sites. Some of the most common materials for hydrogen storage are based on transition metals (TMs). In most of these materials, hydrogen typically occupies tetrahedral interstitial sites. Therefore, the combination of favorable chemical com-

positions and either amorphous or icosahedral structures, which both are dominated by local tetrahedral order, may make the hydrogen absorption/desorption behavior significantly different from that of conventional crystalline alloys. Indeed, quasicrystalline Ti–Zr–Ni [3], as well as amorphous and quasicrystalline Zr–Cu–Ni–Al alloys [4], have been reported to absorb relatively high contents of hydrogen. However, hydrogen release from amorphous and quasicrystalline Zr–Cu–Ni–Al alloys has been found to be inhibited by the presence of a thin oxide layer [5]. To overcome this problem, both melt-spun amorphous and annealed quasicrystalline ribbons have been coated by vapor deposition with a thin layer of palladium (Pd), approximately 100 nm thick. This layer was found to enhance significantly the absorption/desorption behavior of hydrogen in these alloys [6,7]. The aim of this paper is to analyze in detail the different characteristics of deuterium desorption from Pd-coated amorphous and partially quasicrystalline ( $V_{qc} = 50\%$ )  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  alloys. Although Zr–Cu–Ni–Al alloys may not be attractive for hydrogen storage applications, either

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because they are too heavy (resulting in low gravimetric storage capacity) or do not allow desorption at sufficiently low temperatures, they enable the isolation of the effect of microstructure on hydrogen absorption/desorption characteristics. Therefore, this system was selected for study.

## 2. Experimental procedure

Amorphous  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  ribbons were prepared by melt spinning. Partially quasicrystalline ribbons were subsequently formed by annealing amorphous ribbons above the glass transition temperature (367 °C). The icosahedral quasicrystals form at 422 °C and decompose at 467 °C into stable crystalline phases, as described elsewhere in detail [4]. The ribbons were then coated with a 100 nm-thick layer of Pd by vapor deposition. The coating exhibited sufficient adhesion to both ribbons. Deuterium desorption behavior was studied by thermal desorption spectroscopy (TDS), a technique that involves measurement of the desorption rate of gas atoms, dissolved or trapped in the material, while heating the sample at a known rate. For TDS experiments, the ribbons were electrochemically charged at room temperature for different periods, applying a current density of 5 A/m<sup>2</sup> in a 2:1 glycerine: *d*<sub>3</sub>-phosphoric acid (D<sub>3</sub>PO<sub>4</sub>) solution. After ultrasonic cleaning in ethanol, the specimen was placed into its holder, and the system was sealed and pumped down to 10 μPa. The heating rate varied from 3 to 7 °C/min, while the temperature range was 50–600 °C, both parameters being programmed into a temperature controller. The mass spectrometer was operated under a continuous mode to scan atomic masses within the range 3.5–4.5 amu to detect deuterium desorption. Quantification of several trapping parameters was carried out following the procedure described elsewhere [5].

The influence of the absorption and desorption processes on the microstructure was investigated by means of X-ray diffraction (XRD), using a Rigaku Type 2000 X-ray powder diffractometer and a Ni-filtered Cu K $\alpha$  radiation. The amount of residual deuterium inside the specimens after thermal desorption experiments was measured by vacuum extraction, using a LECO RH-404 microprocessor-based system. The system determines hydrogen content in ferrous and non-ferrous materials, using a high power electrode furnace, with an accuracy of  $\pm 0.05$  ppm (or 2% of the reading, whichever is higher). The hydrogen released from the fused sample is swept (with other desorbed gases) by argon carrier gas through a series of filters to a molecular sieve column and, after being separated from the other gases, it is quantified in a sensitive thermal conductivity cell. A more detailed technical description of the LECO system is given elsewhere [7]. The amount of residual deuterium

was also estimated as the subtraction of the integral of the TDS plot from the amount absorbed in the material.

## 3. Results and discussion

### 3.1. The effect of absorbed hydrogen content on the desorption behavior

Typical TDS spectra for Pd-coated amorphous and quasicrystalline  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  specimens are shown in Fig. 1a and b, respectively. In both cases, the specimens were first charged with different deuterium concentrations, applying a constant current density but different charging periods. The amount of deuterium absorbed was determined for each sample by cutting a piece and analyzing it with a LECO hydrogen determinator. The deuterium concentration is expressed herein in terms of D/M, i.e. the deuterium-to-metal atom ratio. It should be noted that the LECO allows measurement

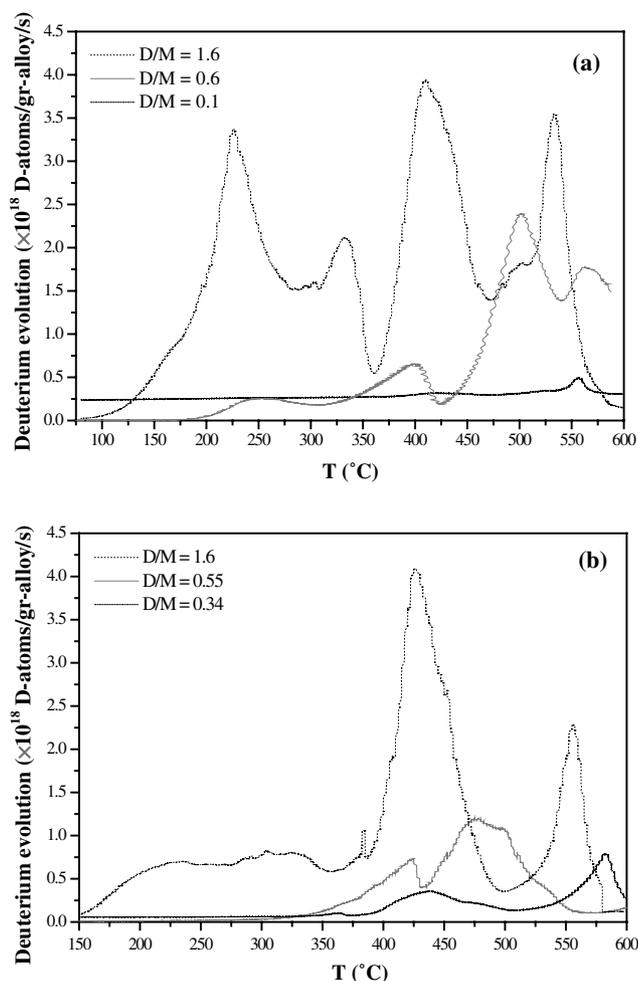


Fig. 1. The dependence of desorption profile on the initial deuterium loading for (a) amorphous, and (b) partially quasicrystalline Pd-coated  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  alloys. All chargings were carried out electrochemically at  $i_c = 5$  A/m<sup>2</sup>.

of either hydrogen or deuterium concentrations, and that the kinetics of deuterium absorption has been reported to be slower [7]. The heating rate (temperature ramp) was kept constant at 5 °C/min. Quantification of several trapping/detrapping parameters is provided in Table 1. As expected, the intensity of desorption peaks increases when the sample is precharged with a higher content of deuterium. 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.

One desorption peak is observed at 557 °C for the amorphous material precharged to 0.1 D/M. However, when the amorphous material is preloaded with 0.6 D/M, four peaks are evident (at 253, 402, 501 and 561 °C). Four peaks (at 225, 332, 410 and 532 °C) are also noticed for the amorphous material preloaded with 1.6 H/M. It is possible that the shoulder on the left side of the four peak (approximately at 500 °C) represents another peak that was not fully deconvolved. Thus, it can be concluded that as the Pd-coated amorphous alloy is charged with higher concentrations of deuterium, the desorption peaks in the TDS spectra are both shifted to lower temperatures and increase in number. In amorphous alloys, such a peak shift to lower temperatures may be explained in terms of occupancy of sites of shallower energy levels in the amorphous structure [8,9]. However, since phase transformations in the Zr–Cu–Ni–Al system take place in parallel to desorption, one may also relate the desorption peaks at higher temperatures to deuterium release during the decomposition of quasicrystals, whose temperature decreases as deuterium content increases. Comparing our TDS results to those

reported on the uncoated alloy [5], the amount of deuterium desorbed from the Pd-coated amorphous 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.

In the case of the partially quasicrystalline alloy, the TDS peaks are also shifted to lower temperatures when the material is preloaded with higher concentrations of deuterium. Here, the shift may be attributed to a higher tendency of deuterium atoms to occupy new trap sites of lower binding energy when more deuterium is introduced into the material. In the case of the quasicrystalline alloy, it is not as clear that the number of desorption peaks increases with increasing deuterium loadings. It should be noted that all peaks appearing at temperatures higher than 470 °C may be associated also with decomposition of the quasicrystalline phase into Zr-based crystalline phases as well as with Zr-based hydride formation [6]. Several significant differences are noticed when comparing the current TDS results for the Pd-coated quasicrystalline alloy to those reported for the uncoated quasicrystalline alloy [5]. The Pd coating allows desorption to start at a much lower temperature, exposes additional desorption peaks, allows a better differentiation between desorption spectra from samples that were charged for different periods under otherwise the same conditions, and allows recovery of most of the deuterium that was loaded into the material. In addition, while the desorption peaks of the Pd-coated samples are shifted to lower temperatures when the material is preloaded with higher concentrations of deuterium, those of uncoated samples were shifted to higher

Table 1

Summary of TDS parameters for Pd-coated  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  amorphous and quasicrystalline alloys as a function of loaded deuterium concentration

Charged deuterium content (D/M)	Temperature at desorption peak (°C)	Maximal desorption rate ( $\times 10^{15}$ D-atoms/s)	Number of clear desorption peaks	Total desorbed deuterium (D/M)
<i>Amorphous alloy</i>				
0.10	557	$6.57 \times 10^{-2}$	1	0.096
0.60	253	$4.56 \times 10^{-1}$	4	0.576
	402	1.30		
	501	4.87		
	561	3.76		
1.60	225	1.05	4	1.40
	332	$6.59 \times 10^{-1}$		
	410	1.23		
	532	1.11		
<i>Quasicrystalline alloy</i>				
0.34	439	$2.90 \times 10^{-1}$	2	0.271
	582	$6.43 \times 10^{-1}$		
0.55	424	$4.97 \times 10^{-1}$	2	0.318
	475	$8.21 \times 10^{-1}$		
1.60	427	2.63	2	1.49
	556	1.46		

Heating rate is 5 °C/min.

temperatures [5]. These differences clearly demonstrate the major role of the oxide surface barrier layer in deuterium desorption from the Zr-based quasicrystalline alloy.

Various studies of hydrogen interaction with amorphous alloys [8,10–13] have shown that hydrogen occupies in these materials trapping sites with a distribution of binding energies that may be related to a distribution of defects. However, to the best of our knowledge, hardly any studies have been reported on hydrogen trapping in quasicrystalline alloys. Possible trap sites in the quasicrystalline Pd-coated  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  alloy could be defects, including dislocations which are inevitably accompanied by strain fields (phason strain) [14]. This strained region may produce more free volume for trapping of small atoms such as hydrogen. Yet, the mechanisms of hydrogen trapping in quasicrystalline materials are still to be determined.

### 3.2. The influence of heating rate on desorption behavior

The influence of heating rate on deuterium desorption was studied by means of TDS, employing various heating rates within the range 3–7 °C/min. Fig. 2a and b reveal the typical heating rate dependence of thermal desorption from amorphous and quasicrystalline specimens, respectively, precharged with 1.6 D/M. Table 2 summarizes several important parameter values. It is noticed that with an increased heating rate, the desorption peaks of either amorphous or quasicrystalline Pd-coated  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  samples are shifted to higher temperatures; in addition, the total amount of desorbed hydrogen is decreased.

At all heating rates, several differences are noticed in the desorption behavior of amorphous versus quasicrystalline alloys. Desorption from the amorphous alloy always starts at a lower temperature in comparison with desorption from the quasicrystalline alloy. This behavior, which was also reported for the uncoated samples [5], may result from higher activation energy for detrapping from the quasicrystalline alloy. In addition, phase transformations may allow deuterium release. In such a case, desorption from the initially amorphous alloy can be expected to start at lower temperatures, as the temperature for the formation of quasicrystals is lower than that for their decomposition.

At heating rates of 3 °C/min and 5 °C/min, desorption from the amorphous alloy begins below 100 °C, whereas desorption from the quasicrystalline alloy begins at approximately 130 °C. This is a significant improvement compared to uncoated amorphous and quasicrystalline alloys, for which desorption started only at 350 °C and 460 °C, respectively (at 5 °C/min) [5]. This emphasizes the great effect of Pd coating, in particular on the quasicrystalline alloy. If the heating rate is increased to 7 °C/min, desorption from either Pd-coated amorphous alloy

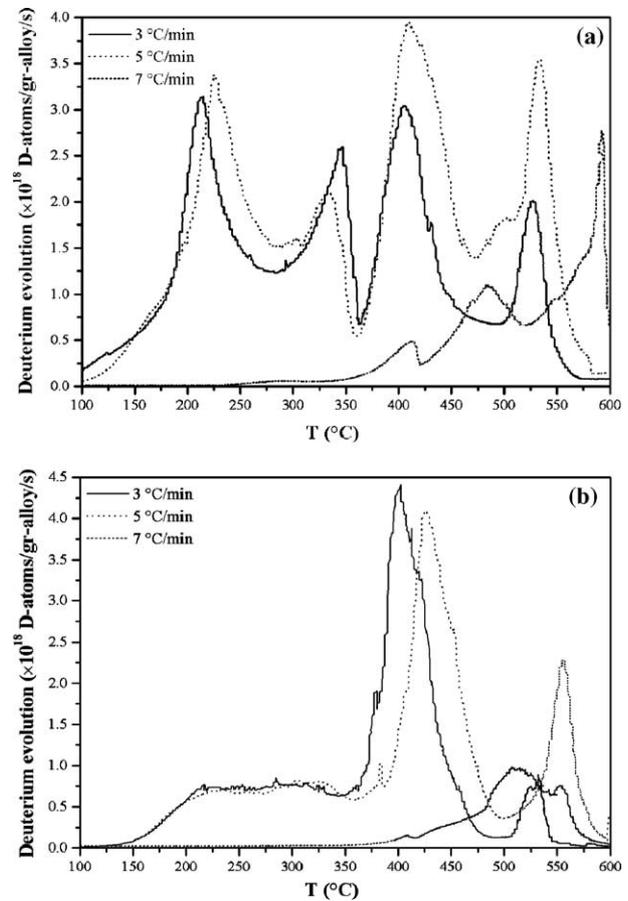


Fig. 2. Heating rate dependence of deuterium evolution from Pd-coated amorphous (a) and quasicrystalline (b)  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  alloys. Electrochemical charging was carried out at  $i_c = 5 \text{ A/m}^2$  to D/M = 1.6.

or Pd-coated quasicrystalline alloy starts at much higher temperatures ( $\sim 250$  °C and  $\sim 350$  °C, respectively). For both materials, much less deuterium can be recovered at the highest heating rate (see Fig. 2 and Table 2). Therefore, it may be concluded that a heating rate of 7 °C/min is too high in the case of the Zr–Cu–Ni–Al system if good recovery of deuterium is required. Finally, it may be noted from Table 2 that either at 3 °C/min or at 5 °C/min, desorption from the amorphous alloy is of the same order of magnitude at each of the four peaks identified. On the other hand, at the same heating rates, the quasicrystalline alloy exhibits one desorption peak at which the amount of desorbed deuterium is about one order of magnitude larger than that at the other peaks. The peak intensity depends on the content of trapped atoms and on the heating rate [15]. Therefore, it may be claimed that the amorphous alloy contains additional kinds of traps with low binding energies and high trap densities as compared to the quasicrystalline alloy. Desorption over a narrower temperature range may be beneficial for hydrogen storage applications.

Applying Kissinger's analysis, the activation energy for deuterium release may be calculated from the slope of  $\ln(\phi/T_p^2)$  versus  $1/T_p$ , where  $\phi$  is the heating rate

Table 2

Summary of TDS parameters for Pd-coated  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  amorphous and quasicrystalline alloys as a function of heating rate

Heating rate (°C/min)	Temperature at desorption peak (°C)	Maximal desorption rate ( $\times 10^{15}$ D-atoms/s)	Number of clear desorption peaks	Total desorbed deuterium (D/M)
<i>Amorphous alloy</i>				
3	215	2.33	4	1.59
	347	1.92		
	405	2.25		
	527	1.49		
5	225	1.05	4	1.40
	332	$6.59 \times 10^{-1}$		
	410	1.23		
	532	1.11		
7	291	$2.97 \times 10^{-2}$	4	0.46
	413	$6.25 \times 10^{-1}$		
	485	1.39		
	593	3.53		
<i>Quasicrystalline alloy</i>				
3	402	3.09	2	1.58
	533	$6.25 \times 10^{-1}$		
5	427	2.63	2	1.49
	556	1.46		
7	409	$8.99 \times 10^{-2}$	3	0.23
	507	$5.90 \times 10^{-1}$		
	552	$4.57 \times 10^{-1}$		

Hydrogenation was to D/M = 1.60.

and  $T_p$  is the peak temperature value [5]. Following this procedure, the activation energy was found to be  $E_{aT} = 2.4$  kJ/mole and  $E_{aT} = 17.7$  kJ/mole for the first peak and second peak, respectively, in the desorption spectra of the Pd-coated quasicrystalline alloy. These values are much lower than the value reported for the uncoated quasicrystalline alloy ( $E_{aT} \sim 37.6$  kJ/mole). However, they are larger than the activation energy values for desorption from different traps in a Pd-coated amorphous alloy that was charged with an identical deuterium content of 1.6 D/M ( $E_{aT} = 1.5, 1.6, 2.7$  and  $5.3$  kJ/mole for the first, second, third and fourth peaks, respectively). It should be noted that these results indicate that the traps in either amorphous or quasicrystalline Zr–Cu–Ni–Al alloys are reversible, because the activation energy values are all much lower than the upper limit value of 60 kJ/mole that was suggested for an edge dislocation, grain boundary, or other reversible traps in steels [16]. It should be realized that the low values of activation energy may also indicate release from common tetrahedral sites. Bankmann et al. [17] have suggested a new model which predicts the behavior of hydrogen in multi-component amorphous alloys. These authors show that in a four-constituent alloy such as  $Zr_{66.6}Al_{17.4}Ni_{7.2}Cu_{8.8}$ , 35 types of tetrahedra are available for hydrogen occupancy. Even when blocking due to repulsive interaction between two neighbor hydrogen atoms is accounted for, the variety of tetrahedra still results in several peaks located at different heat of solutions in the plot of density of sites. Because the icosahedral structure is also dominated by local tetrahedral

structure, a similar behavior of desorption from different tetrahedra may apply.

### 3.3. The influence of the absorption/desorption processes on the microstructure

In order to investigate the effect of deuterium desorption at various heating rates (3, 5 and 7 °C/min) on the microstructure of Pd-coated amorphous and quasicrystalline  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  alloys, both alloys were first charged with an equal deuterium concentration D/M = 1.6. TDS was subsequently employed within an identical temperature range of 30–600 °C, and was followed by XRD experiments. Typical data are shown in Fig. 3.

The XRD patterns consist of peaks of the tetragonal  $Zr_2Cu$ , tetragonal  $Zr_2Ni$  and cubic Pd phases, the latter being clearly originated with the coating. In contrast to the previously reported XRD patterns after DSC at 550 °C [6], no Zr-hydride phases are identified here. This may mean that in the present work, no hydrides could form, or that either decomposition of existing hydrides or complete desorption of deuterium before any new hydrides started forming took place. Indeed, TDS data shows that most of the absorbed deuterium could be recovered from either the amorphous or quasicrystalline alloys when heating was applied at either 3 °C/min or 5 °C/min. However, when heating at 7 °C/min, only 14.4% and 28.8% of the absorbed hydrogen was released from the quasicrystalline and amorphous alloys, respectively. Furthermore, desorption took place mainly at high temperature. These results support the speculation that

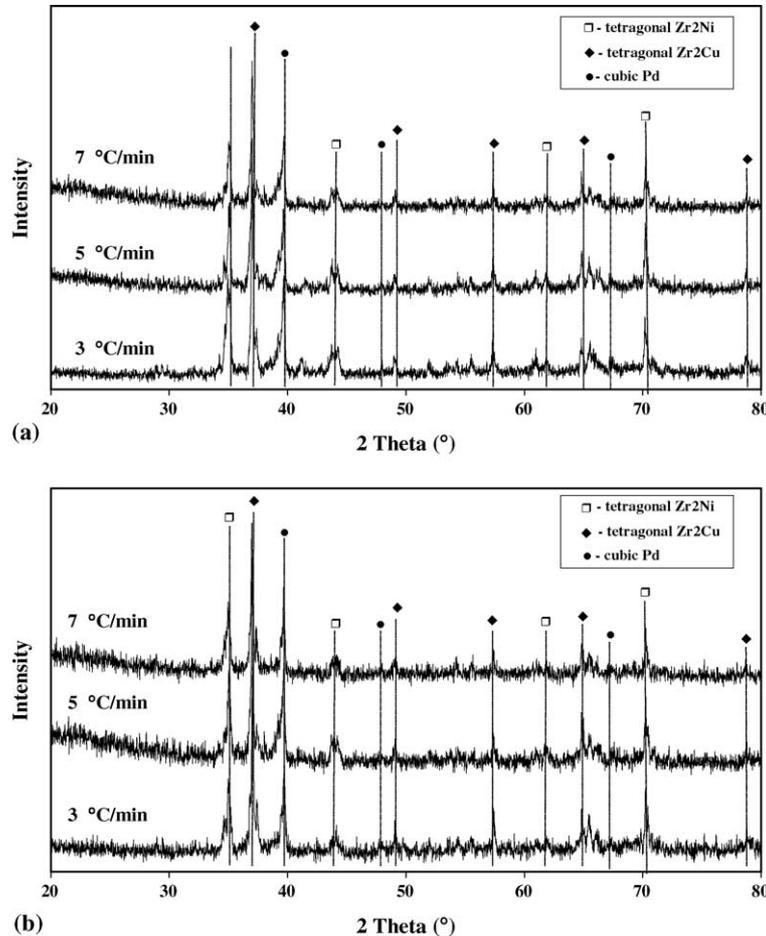


Fig. 3. X-ray diffraction patterns of hydrogenated Pd-coated amorphous (a) and quasicrystalline (b)  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  alloys following desorption from 30 to 600 °C. All samples were first charged electrochemically at  $i_c = 5 \text{ A/m}^2$  to  $D/M = 1.6$ . Note the different heating rates applied in TDS.

the absence of hydride phases in the XRD patterns is related to decomposition of existing hydrides at elevated temperatures. Similar behavior was reported [18] for hydrogenated  $Zr_{55}Cu_{30}Al_{10}Ni_5$  metallic glass and hydrogen concentrations within the range  $0.7 < H/M < 1$ .

#### 4. Conclusions

Based on the results of this work, the following conclusions may be drawn:

- (1) The characteristics of deuterium desorption from Pd-coated amorphous and quasicrystalline  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  alloys are affected by the presence of different trapping sites in either structure, as well as by decomposition of either the matrix or Zr-based hydrides.
- (2) Deuterium release from the amorphous alloy begins at lower temperatures in comparison to the quasicrystalline alloy. This behavior probably results from traps with higher binding energy in the quasi-

crystalline structure, although it may also be influenced by phase transformations that occur during heating.

- (3) The palladium coating enables a better recovery of deuterium from either amorphous or quasicrystalline Zr–Cu–Ni–Al alloys. In addition, it significantly changes the desorption behavior from the quasicrystalline alloy.
- (4) While heating rates of 3 °C/min and 5 °C/min allow recovery of most of the charged deuterium, a heating rate of 7 °C/min is too high for the Zr–Cu–Ni–Al system and results in both poor recovery and shift of desorption to much higher temperatures.

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