

# Hydrogen absorption in intermetallic alloys type $\text{LaNi}_5$ and $\text{ZrNi}_5$

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**Abstract** A method of electrochemical desorption of hydrogen from a cylinder-shape specimen was used for the determination of the effective diffusion coefficient of hydrogen in  $\text{LaNi}_5$ ,  $\text{LaNi}_{4.8}\text{Sb}_{0.2}$ ,  $\text{Zr}_{0.8}\text{La}_{0.2}\text{Ni}_5$ , and  $\text{ZrNi}_{4.8}\text{Al}_{0.2}$  alloys, previously saturated with hydrogen produced electrochemically. Then the concentrations of diffusible hydrogen and of hydrogen derived from hydride phases were determined.

**Keywords** *Hydrogen absorption, diffusion, desorption,  $\text{LaNi}_5$ ,  $\text{LaNi}_{4.8}\text{Sb}_{0.2}$ ,  $\text{Zr}_{0.8}\text{La}_{0.2}\text{Ni}_5$ ,  $\text{ZrNi}_{4.8}\text{Al}_{0.2}$*

## Introduction

Intermetallic alloys which are able to reversibly absorb and desorb considerable amount of hydrogen are being used or considered for variety energy applications [1-3]. The most interesting are  $\text{LaNi}_5$  and  $\text{ZrNi}_5$  due to their large hydrogen capacity and good absorption/desorption kinetics under room conditions. The demand for improved performance of such materials (higher absorption capability as well as lower susceptibility to hydrogen degradation) promotes research on the storage of hydrogen by the intermetallic alloys with various chemical compositions.

Since the intermetallic alloy-hydrogen systems are complex, they are difficult to study. For instance, hydrogen in  $\text{LaNi}_5$  alloy can occur as  $\alpha$ -phase (low concentrated solution of hydrogen in the metal lattice,  $\text{LaNi}_5\text{H}_{0.5}$ ),  $\beta$ -phase (hydride  $\text{LaNi}_5\text{H}_3$ ),  $\gamma$ -phase (hydride  $\text{LaNi}_5\text{H}_6$ ) [4,5], as well as hydrogen attached to various structural defects, *i.e.* the so-called trapped hydrogen. Moreover, the quantity of the structural defects increases in time as a consequence of high deformation of the metal lattice accompanying to the formation and decomposition of hydride phases. Therefore, it is not easy to characterize

unambiguously the behaviour of hydrogen in such systems, especially to determine the mobility, concentration and distribution of hydrogen among the metal lattice, hydride phases, and traps.

The objective of this work was to examine and compare the behaviour of hydrogen in  $\text{LaNi}_5$ ,  $\text{LaNi}_{4.8}\text{Sb}_{0.2}$ ,  $\text{Zr}_{0.8}\text{La}_{0.2}\text{Ni}_5$  and  $\text{ZrNi}_{4.8}\text{Al}_{0.2}$  subjected to cathodic charging.

### **Material and applied method**

The materials used were prepared by melting of stoichiometric amounts of the spectral pure metals (99.99%) in an argon atmosphere. The obtained ingots were homogenized under vacuum in 600 °C for 300 h.

Since the obtained alloys had structural discontinuities (holes, crevices), it was not possible to use a very convenient electrochemical permeation technique [6] based on the permeation of hydrogen through a thin membrane. In this situation, a little less informative but also suitable electrochemical technique [7], based on the desorption of hydrogen from a cylindrical specimen previously uniformly saturated with hydrogen [8], was applied.

The preparation of quite small specimens in the shape of thin cylinder, suitable for electrochemical measurements was difficult, because the ingots were very hard (especially alloys with Zr) and brittle. The specimens were cut from ingots using thin diamond disk and subsequently were grinded down using diamond grinding arbor. The prepared specimens had a nearly cylindrical shape. A typical specimen looked like that shown in Fig. 1. Dimensions of the prepared specimens are given in Table 1.

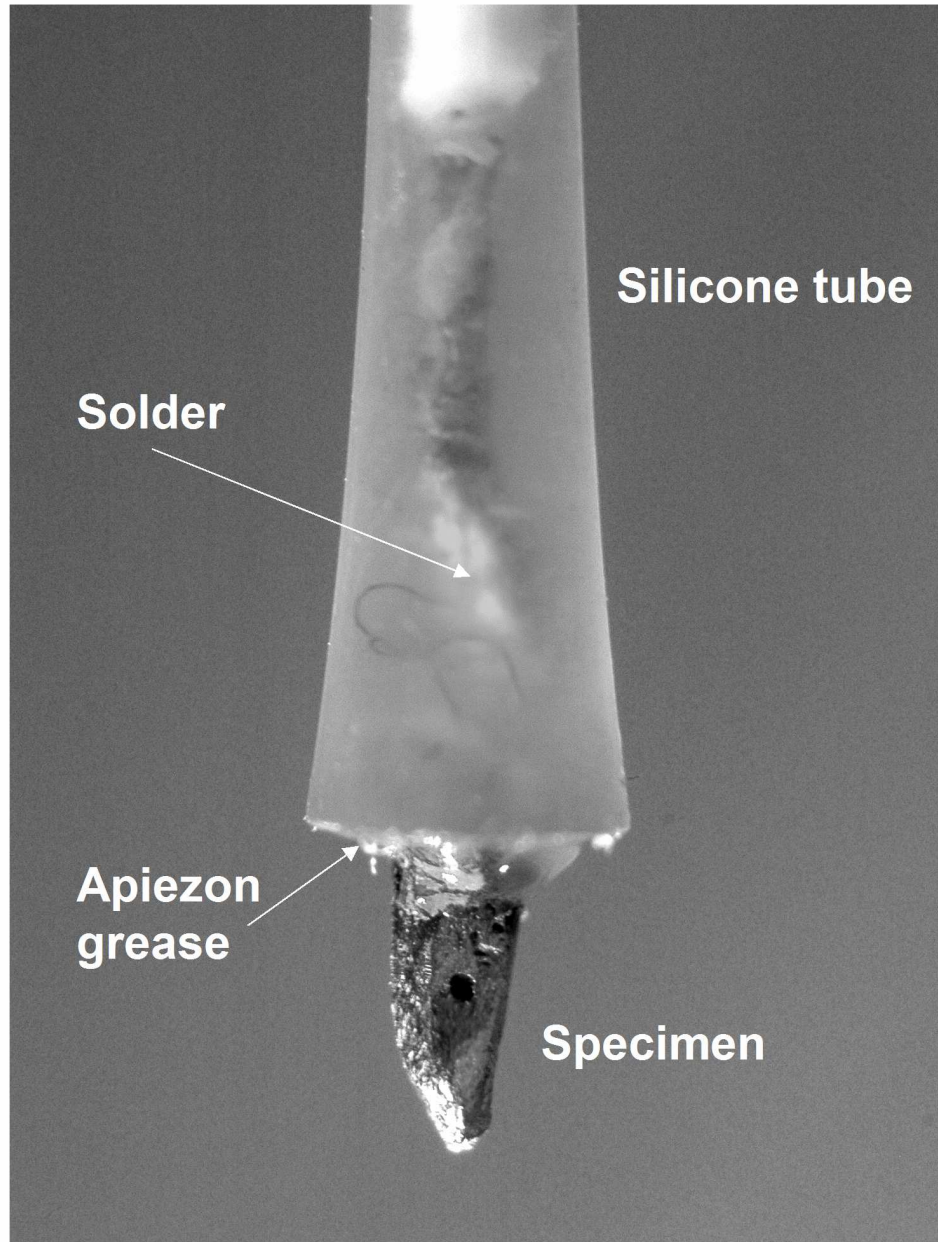


Fig. 1 The specimen prepared for electrochemical measurements

Alloy	Length $L$ (mm)	Radius $R$ (mm)	Area $A$ (mm <sup>2</sup> )	Volume $V$ (mm <sup>3</sup> )
LaNi <sub>5</sub>	2.5	0.54	9.46	2.30
LaNi <sub>4.8</sub> Sb <sub>0.2</sub>	2.9	0.62	12.53	3.52
Zr <sub>0.8</sub> La <sub>0.2</sub> Ni <sub>5</sub>	3.5	0.65	15.74	4.68
ZrNi <sub>4.8</sub> Al <sub>0.2</sub>	2.3	0.50	8.15	1.84

Table 1 Dimensions of the prepared cylindrical specimens

The specimens were cathodically charged with hydrogen in 0.1 M NaOH under a relatively low current density  $i_c = 75 \mu\text{A}/\text{cm}^2$ . After sufficiently long time (about 400 h) the hydrogen charging was switched off and the specimen was immediately subjected to anodic polarization in the same solution under a constant electrode potential of  $-0.34 V_{\text{Hg|HgO|0.1 M NaOH}}$  ( $-0.18 V_{\text{SHE}}$ ). This potential was chosen on the base of the polarisation curve measurements and it provided an efficient oxidation of hydrogen atoms. However, the measured anodic current  $I_a$  consists of two components

$$I_a = I_H + I_{Me} \quad (1)$$

where:  $I_H$  is the current corresponding to the oxidation of hydrogen atoms desorbing from the specimen, and  $I_{Me}$  is the current related to other possible anodic processes, including those of dissolution and passivation of the alloy. Therefore, the current  $I_{Me}$  made the so-called background current and it had to be determined in the separate measurement on the hydrogen-free specimen. The electrochemical measurements were carried out at  $30^\circ\text{C}$  in the 0.1 M NaOH solution deaerated with argon.

## Results and Discussion

The overall desorption rates of hydrogen  $I_H$  from the examined specimens are shown in Fig. 2. One can note that after a sufficiently long time, the logarithm of  $I_H$  becomes approximately linear function of time.

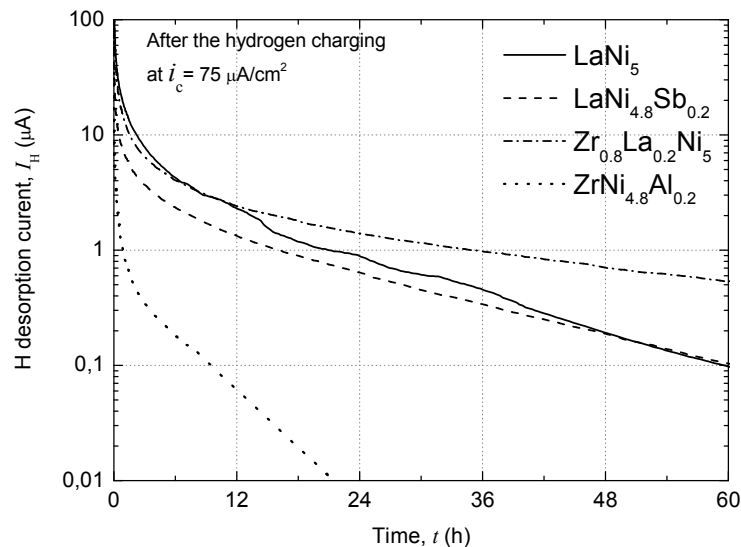


Fig. 2 The desorption rate of hydrogen  $I_H$  from different specimens cathodically charged with hydrogen

This suggests, that in this period of time the desorption rate of hydrogen was controlled only by its diffusion in the alloy. Assuming that the initial concentration of that so-called diffusible hydrogen ( $I_{Hd}$ ) was uniform, its desorption rate is given by the following equation [7,8]

$$I_{Hd} = \frac{4Q_{Hd}^0 D}{R^2} \left\{ \exp\left[-\frac{D(2.405)^2 t}{R^2}\right] + \exp\left[-\frac{D(5.520)^2 t}{R^2}\right] + \exp\left[-\frac{D(8.654)^2 t}{R^2}\right] + \dots \right\} \quad (2)$$

where:  $Q_{Hd}^0$  is the initial amount of diffusible hydrogen in the charged specimen,  $D$  is the diffusion coefficient,  $R$  is the specimen radius, numerical coefficients are successive roots of the Bessel's function of the first kind of zero order, and  $t$  is time.

Fitting the equation (2) to the linear section of the  $\log(I_H) - t$  curve, the diffusion coefficient  $D$  and the amount of diffusible hydrogen  $Q_{Hd}^0$  can be evaluated. In turn, knowing values of  $D$  and  $Q_{Hd}^0$ , one can reconstruct the desorption rate of diffusible hydrogen  $I_{Hd}$  in the whole range of time. As an example, Fig. 3 shows the analysis of the desorption rate of hydrogen from the  $Zr_{0.8}La_{0.2}Ni_5$  specimen.

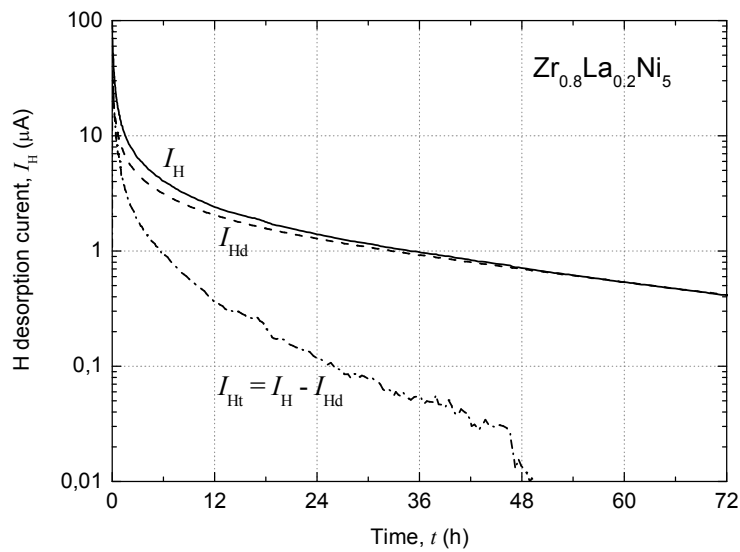


Fig. 3 Decomposition of the overall desorption rate ( $I_H$ ) into the desorption rate of diffusible hydrogen ( $I_{Hd}$ ) and hydrogen derived from hydride phases ( $I_{Ht}$ );  $Zr_{0.8}La_{0.2}Ni_5$  specimen

It is seen, that in the initial period of time the overall desorption rate  $I_H$  was higher than the calculated desorption rate of diffusible hydrogen  $I_{Hd}$ . Their remainder  $I_{Ht}$  gives the desorption rate of hydrogen derived formally from traps, but undoubtedly it mainly concerned hydrogen derived from the decomposed hydride phases.

Integration of the relevant currents  $I_H$ ,  $I_{Ht}$ , and  $I_{Hd}$  gives electric charges, corresponding to the total amount of hydrogen in the specimen  $Q_H$  and the partial amounts of different forms of hydrogen:  $Q_{Hd}$  and  $Q_{Ht}$ . Taking into account different dimensions of specimens and assuming that hydrogen was previously evenly distributed within the specimen, the more objective, average molar concentrations of hydrogen  $C_H$  and the concentrations of corresponding forms:  $C_{Hd}$  and  $C_{Ht}$  were calculated (Table 2 and Fig. 4).

Alloy	Diffusion coefficient $D \times 10^9$ ( $\text{cm}^2/\text{s}$ )	Hydrogen charge (mC)			Average concentration (mol H/dm <sup>3</sup> )		
		$Q_H$	$Q_{Hd}$	$Q_{Ht}$	$C_H$	$C_{Hd}$	$C_{Ht}$
LaNi <sub>5</sub>	8,7	484,8	323,3	161,5	2,18	1,45	0,73
LaNi <sub>4,8</sub> Sb <sub>0,2</sub>	9,2	242,4	210,1	32,3	0,71	0,62	0,09
Zr <sub>0,8</sub> La <sub>0,2</sub> Ni <sub>5</sub>	4,3	574,5	467,9	106,6	1,27	1,04	0,23
ZrNi <sub>4,8</sub> Al <sub>0,2</sub>	21,8	19,8	15,5	4,3	0,11	0,09	0,02

Table 2 Hydrogen diffusion coefficients, hydrogen charges, and the average concentrations of different forms of absorbed hydrogen

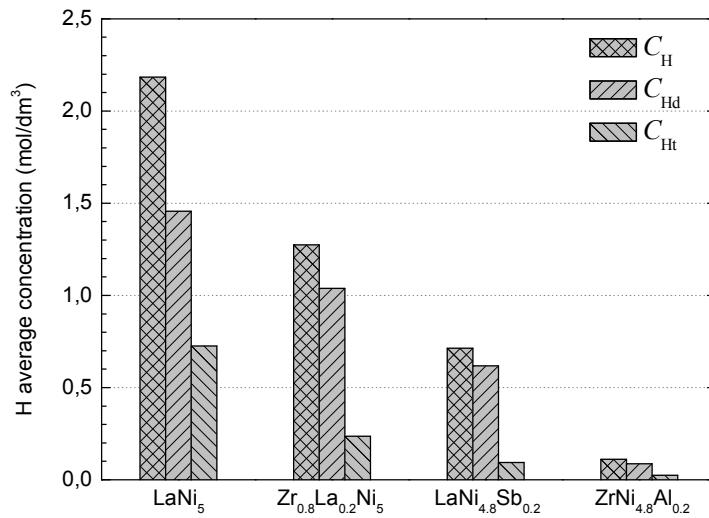


Fig. 4 The average concentration of different forms of hydrogen in alloys subjected to the cathodic charging at the same current density  $75 \mu\text{A}/\text{cm}^2$

The obtained results shows that the ability to storage of hydrogen in the alloys decrease in the following order LaNi<sub>5</sub>, Zr<sub>0.8</sub>La<sub>0.2</sub>Ni<sub>5</sub>, LaNi<sub>4.8</sub>Sb<sub>0.2</sub>, and ZrNi<sub>4.8</sub>Al<sub>0.2</sub>. Similarly, the equilibrium concentrations of the both forms of hydrogen (diffusible hydrogen and hydrogen in hydrides) also decrease in the same order. The basic LaNi<sub>5</sub> alloy seems to be better than other examined alloys at the applied mild conditions of hydrogen charging. Moreover, LaNi<sub>5</sub> alloy has the strongest tendency to form hydride phases which results in a beneficial higher current density in the initial period of time. On the other hand, as it was shown in [9], LaNi<sub>5</sub> is more susceptible than Zr<sub>0.8</sub>La<sub>0.2</sub>Ni<sub>5</sub> to hydrogen degradation and it can be charged without degradation (pulverisation) only at relatively low cathodic current density,  $i_c < 400 \mu\text{A}/\text{cm}^2$ . In consequence, some more resistant alloys can be more electrochemically saturated with hydrogen than LaNi<sub>5</sub> at higher charging current densities.

The total concentrations of hydrogen in the alloys can be express as the following formulas: LaNi<sub>5</sub>H<sub>0.112</sub>, Zr<sub>0.8</sub>La<sub>0.2</sub>Ni<sub>5</sub>H<sub>0.059</sub>, LaNi<sub>4.8</sub>Sb<sub>0.2</sub>H<sub>0.038</sub>, and ZrNi<sub>4.8</sub>Al<sub>0.2</sub>H<sub>0.005</sub>. It shows, that the saturation of alloys after the cathodic charging at  $i_c = 75 \mu\text{A}/\text{cm}^2$  was relatively low and, theoretically, it corresponded with  $\alpha$ -phase (low concentrated solid solution of hydrogen). However, in the initial period of time, the overall desorption current was higher than that predicted for

the diffusible hydrogen. It suggests that in these alloys the hydride phases formed and decomposed relatively easily and coexisted with the solid solution of hydrogen.

Finally, it is worthy to underline that in spite of the complexity of the metal-hydrogen system studied, the applied electrochemical method [7] enabled to determine the effective diffusion coefficient of hydrogen and then the concentration of the diffusible hydrogen and of the hydrogen derived from hydrides. However, it was possible that some amount of hydrogen was strongly bonded with some structural defects, and it could be considered as the irreversibly trapped hydrogen (under room temperature).

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