Electric current stimulation of hydrogen diffusion through an amorphous palladium membrane

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The work presents the results of the diffusion of hydrogen through a membrane made of amorphous palladium alloy in which one of the surfaces was modified with a layer of carbon nanotubes. We used an amorphous membrane made with a single roller spinning technique. The measurements were performed at ambient temperature. In this work, an attempt was made to study the impact of the flow of electric charge on the diffusion of hydrogen through thus modified amorphous palladium alloy membrane.

1. Introduction

Palladium membranes and palladium-containing alloys are highly permeable and selective for hydrogen diffusion. This makes them an attractive material for applications in the membrane reactors, fuel cells, as well as sensors and analyzers, gas mixtures containing hydrogen [1, 2]. Pure palladium is well known for its high permeability for hydrogen but its high cost limits its use considerably on an industrial scale. Current research focuses on the exploration of its alloys with other elements and on a modification of their structure and surface to get at least a similar effect as the hydrogen permeability of pure palladium. The basic factors determining the diffusion of hydrogen in the membrane are differential pressure ΔP on both membrane sides and temperature T, but it was repeatedly shown that the diffusion process is strongly dependent on condition of the membrane surface.

On the basis of surface potential measurements [3], it was pointed out that hydrogen adsorbed on the palladium surface can occur in two different forms. Electronegative hydrogen form β^- forms and predominates in the range of low concentrations of

hydrogen on the metal surface. This results from conformation of hydrogen creating dipole with negative side directing from the surface. It is a stable form. The second, electropositive form β^+ of hydrogen is induced from the β^- form in conditions of higher hydrogen concentrations on the membrane surface. The formation of β^+ was described by GRIMLEY [4] on the basis of the theory of quantum mechanics. When the concentration of hydrogen increases on the palladium surface, energy levels of adsorbate electrons split and the band is being formed. Above a certain critical concentration the widening band puts on the conduction band of palladium enabling transition of adsorbate electrons into metal. Therefore, β^+ hydrogen form can be interpreted, with certain approximation, as a positive hydrogen ion – a proton. An important consequence of the loss of an electron, besides the loss of electroneutrality is a significant change of adsorbate dimension. Formed on the surface membrane the electropositive adsorbate β^+ diffuses under the surface as a result of the difference of concentrations. This is a significant difference in the behavior of adsorbate occurring between the two forms of hydrogen. The aim of the present work was to accelerate the process of chemisorption of hydrogen in phase β^+, and consequently the diffusion of hydrogen through the membrane. We have found that polarized connector was created between a layer of carbon nanotubes and the surface membrane.

2. Experimental procedure

In order to eliminate the hydrogen diffusion processes along grain boundaries and the like, use was made of amorphous alloy $Pd_{33}Ni_{52}Si_{15}$. The alloy on the membrane of width 25 mm and 30 μm in thickness was prepared with a single roller spinning technique [5]. A disc of 24 mm in diameter was cut from this tape. The surface of the membrane was examined in terms of structure and composition. X-ray diffraction pattern using Cu Kα radiation had no sharp peak but a broad peak around $2\theta = 43.8°$ proving that it was amorphous. XRD pattern is presented in Fig. 1.

The composition of the alloy was verified by X-ray microanalyzer WDS (wavelength dispersive spectrometry) – see the Table.
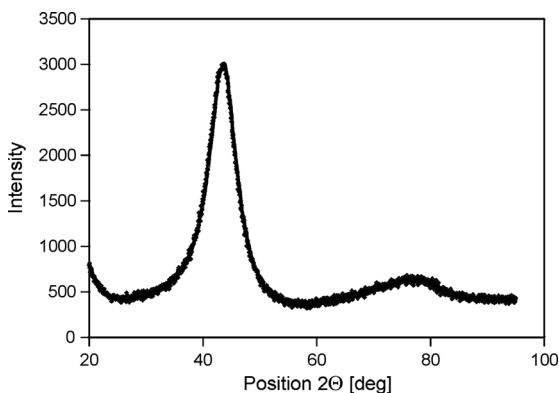

Fig. 1. XRD pattern of the $Pd_{33}Ni_{52}Si_{15}$ amorphous membrane.

T a b l e. Chemical composition of the alloy.

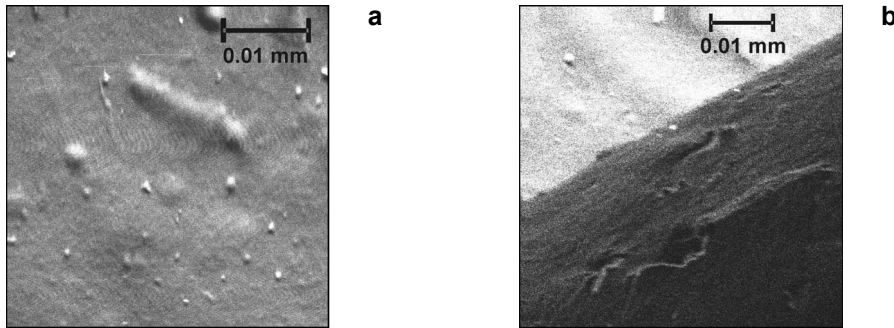| Element	Wt. [%]	At. [%]
Si K	6.17	15.46
Ni K	41.77	50.09
Pd L	52.07	34.45

Fig. 2. SEM image of the surface of carbon nanotubes (**a**), and SEM image showing the edge of the layer of nanotubes (**b**).

One of the membrane surfaces was modified by applying a layer of sedimentary carbon nanotubes (Multiwall Carbon Nanotubes CTube$_{-100}$). This layer was imposed centrally on the surface of the prepared alloy disc and had a thickness of about 0.1 mm and diameter 18 mm. Thus prepared sample was placed in the measuring chamber. The surface layer of nanotubes is shown in Fig. 2**a**, while Fig. 2**b** shows the edge of the layer of nanotubes (a clear field indicates the surface and the dark field shows the side wall).

A diagram of the measuring system for investigation of the hydrogen diffusion through the membrane is shown in Fig. 3. The convention of nomenclature used throughout the text is also marked in this figure.

The measuring chamber constructed in the shape of a cylinder is composed of two parts, separated by a hermetically test sample. The membrane surface with a layer
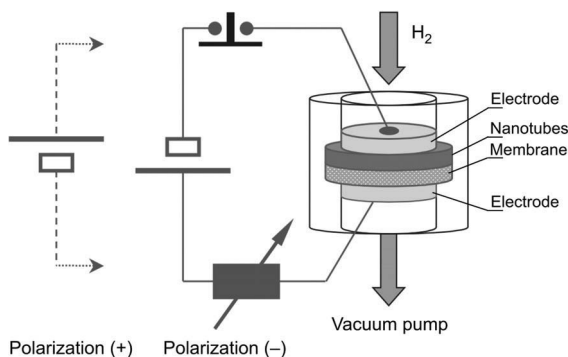

Fig. 3. Membrane module for permeation test.

of nanotubes was in the upper chamber. The upper chamber was filled with hydrogen (purity of 99.999%) at atmospheric pressure while the lower chamber was kept in a vacuum. Two electrodes in the form of a dense grid of copper wires were applied to the membrane surface, so that the current area of contact was as large as possible. The porous structure of carbon nanotubes was readily permeable to hydrogen. During the measurements the sample was kept at room temperature. The measurements of the diffusion of argon 99.999% and air confirmed that there did not exist the penetration of gas through the channels, microporous and other mechanical defects in the membrane. Control measurements of equilibrium pressure of hydrogen diffusion through the $Pd_{33}Ni_{52}Si_{15}$ membrane without the layer of nanotubes and without imposing current to the electrodes were made. In both cases, no significant changes were recorded in the final pressure in the lower chamber where there was a vacuum gauge sensor. Since the pumping speed of the system was fixed and known, the measured value of residual pressure in the chamber can be considered as the rate of diffusion of hydrogen by the sample. After stabilization of pressure in the lower chamber at a constant level of 10^{-4} Pa, the electric current of constant intensity was passed through the membrane. In subsequent cycles, the measured intensity of electric current was changed from 0.1 to 0.5 A. In each cycle of measurements, the electrode polarization was changed (Fig. 3) and the corresponding equilibrium pressure recorded. An important technical problem was to provide the containment chamber.

3. Results and discussion

In order to determine which connector resistance is formed from layers of amorphous carbon nanotubes and membranes, in the first phase of the experiment, the current-voltage characteristics were made. In an inert atmosphere, the characteristics
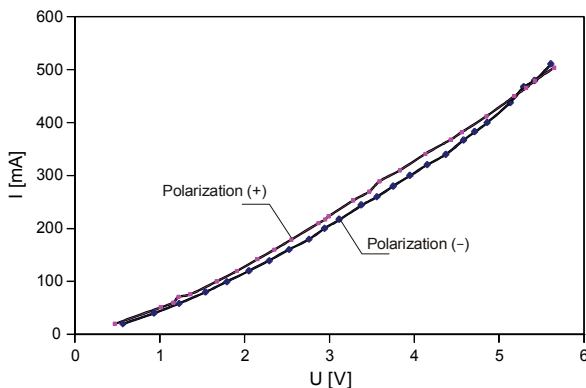

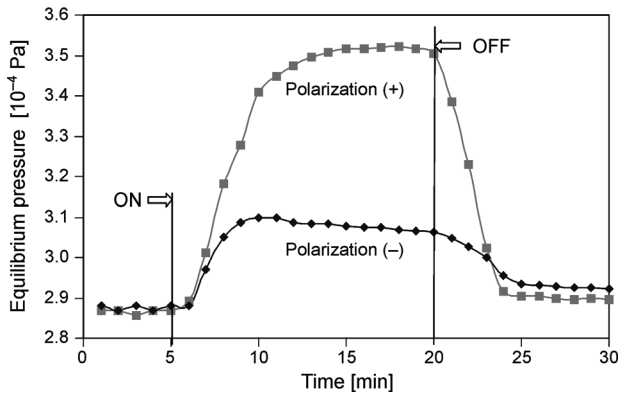Fig. 4. I/U characteristic during permeation of hydrogen through the membrane.

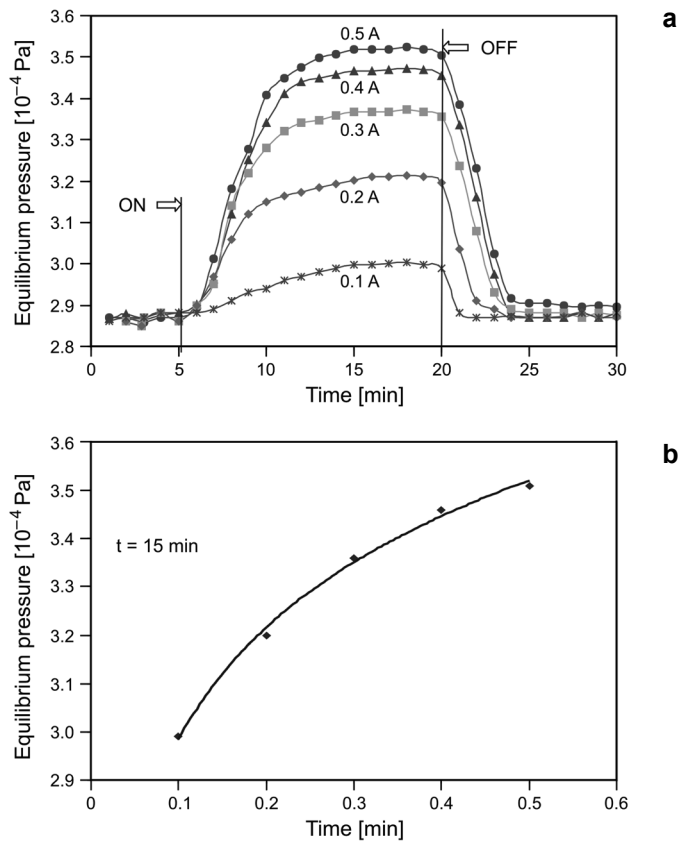Fig. 5. The change in pressure as a function of time, effect of saturation.

Fig. 6. The change in pressure under the influence of current (**a**). Influence of the current intensity in the lower chamber on the equilibrium pressure (**b**).

were well balanced for both directions of current flow, while in the presence of hydrogen they showed a slight asymmetry, as presented in Fig. 4.

Up to the voltage of 5V, the value of current flowing in the direction of hydrogen diffusion in the polarization (+) was somewhat higher. In the remainder of the experiment, the diffusion of H_2 was measured for two opposite polarity currents flowing through the membrane. An example of a change of equilibrium pressure in the lower chamber after a ± 0.5 A change of the current density is given in Fig. 5. The ON/OFF markings indicate the moment of inclusion and exclusion of current, respectively.

Switching on the polarization current (+) has much greater impact on the diffusion of hydrogen through the membrane as compared with diffusion in the polarization (–). Also, the course of the changes is different in both cases. The positive polarization of the hydrogen diffusion through the membrane increases rapidly and remains stable at a high level compared with the diffusion before turning the electricity on (Fig. 6**a**). However, in the negative polarity after switching off the current, the registered effect of diffusion is smaller, there also exists a phenomenon of constant decrease in hydrogen permeation. Switching off the power for this negative polarization causes a small decrease of diffusion and the equilibrium pressure is stabilized at a higher level after switching off the positive polarization.

The relationship between the equilibrium pressure of hydrogen and the current intensity for positive polarity can be described by a logarithmic function (Fig. 6**b**) with good correlation coefficient for the selected time of measurement, for example, for $t = 15$ min R^2 equals 99.63%.

4. Conclusions

Based on the results presented we can formulate the followng conclusions:

– We did not find diffusion of hydrogen by amorphous alloy membrane $Pd_{33}Ni_{52}Si_{15}$ at room temperature.

– The mere imposition of one of the membrane surface layers of carbon nanotubes did not cause changes in the diffusion of hydrogen through the membrane, while flowing through this connector the electric current caused an increase in diffusion of H_2.

– Polarized membrane showed high permeability of hydrogen appropriate for alloys of palladium with VIII group metals.

– A membrane with one layer of surface modified carbon nanotubes for hydrogen diffusion had different resistance to opposing directions of the flow of electric current.

– Polarization of electric current passing through the connector membrane – carbon nanotubes, had an important impact on the diffusion rate. Diffusion of hydrogen was greater during the test in the polarization (+) in comparison with the polarization (–).

– There was found a significant influence of the state of surface membrane on the process of hydrogen diffusion. This process may be modified by creating a polarized connector.

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