Effect of surface coating
with palladium on hydrogen permeability
of $Pd_{33}Ni_{52}Si_{15}$ amorphous alloy membrane

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In the paper, the effect of the surface coating with palladium on hydrogen permeation of
a $Pd_{33}Ni_{52}Si_{15}$ amorphous alloy membrane was investigated. We have measured the hydrogen flow
through the melt-spun amorphous membrane covered with palladium film of 10, 20, and 30 nm in
thickness. Membranes have been tested in the temperature rage 294–358 K, and at pressure fixed
at 102 kPa. We investigate the role of this film thickness on the activation energy for hydrogen
permeability. It seemed that a relatively thin layer of the palladium on the surface of the membrane
which contains over 30% of this element, should not considerably influence the permeability of
the membrane for hydrogen. The membrane hydrogen permeability is correlated to permeation ac-
tivation energy: the lower activation energy is, the higher permeability is observed. The activation
energy for permeation strongly depends on palladium film thickness. The rapid increase of its value
was recorded when the film thickness was growing up. As the result, the increase of the film thick-
ness suppressed hydrogen permeability. Our findings are discussed in terms of a potential barrier
between the two different phases.

Keywords: permeability, hydrogen, palladium alloys, metallic glasses.

1. Introduction

Successive depletion of the conventional energy resources and existing greenhouse gas
emission reductions resulted in an increased interest in hydrogen energy. However,
practically no hydrogen is present in nature in free form. Though it is abundant in chem-
ical compounds such as water and hydrocarbons. One of the fundamental problems that
need to be solved in the process of obtaining hydrogen with a high degree of purity is

to find highly efficient and selective membranes. Membranes composed of palladium or alloys containing palladium are highly penetrating and selective for the permeation of hydrogen which makes them an attractive material for use in this process [1, 2]. However, the high cost of palladium significantly limits its use on an industrial scale. Therefore, searching for the membranes of palladium alloys with other elements and investigations into the modification of their structure and surface, in order to obtain at least the same permeability properties as for hydrogen through pure palladium, are necessary. A very promising method is the modification of a palladium membrane by vapour coating with one or two thin layers of other metal [3, 4]. In our experiments we investigated the influence of presence of a vapour deposited palladium layer on metallic glass $Pd_{33}Ni_{52}Si_{15}$ on its hydrogen permeability.

2. Experimental procedure

An amorphous tape of $Pd_{33}Ni_{52}Si_{15}$ alloy, 25 mm in width and 50 µm in thickness, was prepared with a roller melt spinning method. The amorphicity of the alloy was confirmed by using X-ray microanalyzer as well as by X-ray diffractometry (measurement parameters: Cu Kα, 40 kV, 30 mA). The electron microscopy (SEM) method was employed in order to verify the chemical composition of the alloy. Thermal stability of an amorphous phase was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. No changes in sample structure were noticed at temperatures below 718 K. A disc with a diameter of 24 mm was cut from the tap and put into an analysis chamber. A schematic diagram of the analysis chamber along with the pumping station is depicted in Fig. 1.

Hydrogen diffusion flow through the amorphous membrane coated with palladium was measured using a quadrupole mass analyzer RCA 100 (measurements of partial
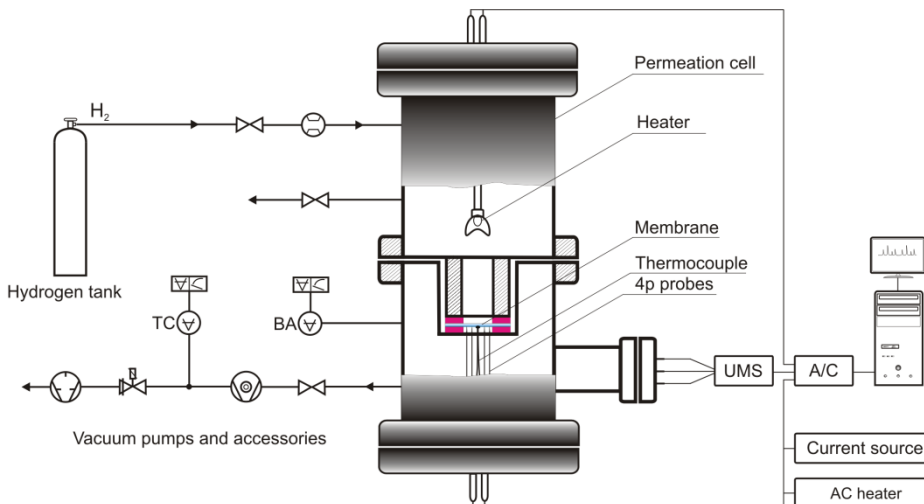

Fig. 1. Test equipment for measuring hydrogen permeation.

pressure), employing the method described elsewhere [5–7]. The changes in hydrogen flow were measured at the temperature range 294–358 K, and at pressure fixed at $p_{out} = 102$ kPa. The initial pressure in the analysis chamber was 1×10^{-6} Pa. Palladium layers of 10, 20 and 30 nm in thickness were evaporated onto one of the membrane surfaces by using an electron beam technique. The thickness of the evaporated layer was measured by quartz crystal microbalance.

3. Results and discussion

The gas flow diffused into through the membrane with a thickness d (in one dimension) should be consistent with Fick's first law of diffusion

$$J_x = -D_x \frac{\partial c}{\partial x} \tag{1}$$

where D_x is the diffusion coefficient of the gas in the membrane, c is the concentration of the amount of gas inside the body while x is the distance from the surface. Concentration, absorbed at the surface of a solid gas is determined by the law of Henry

$$c = K p^u \tag{2}$$

where K is the solubility of the gas and u is the constant that specifies the dissociation of gas (1 or 0.5). The relationship between gas pressure and the quantity of dissolved gas in metal, when the gas is dissociated (as in the case of hydrogen, $u = 0.5$), is determined by the Sieverts law. Therefore, the hydrogen concentration at the boundary surfaces of the membrane is

$$c_1 = K \sqrt{p_{out}} \quad \text{and} \quad c_2 = K \sqrt{p_{in}} \tag{3}$$

and integrating the Eq. (1)

$$J_x \int_0^d dx = -D_x \int_{c_1}^{c_2} dc \tag{4}$$

we get

$$J_x = D_x K \frac{\sqrt{p_{out}} - \sqrt{p_{in}}}{d} \tag{5}$$

The product of $D_x K = P$ is called the permeability. Because the product depends exponentially on the temperature, we can write

$$P = P_0 \exp\left(-\frac{E_p}{kT}\right) \tag{6}$$

where P_0 is the constant of gas permeability and E_p is activation energy in the process. In our experiment $p_{out} \gg p_{in}$, which allows you to save the Eq. (5) more simply:

$$J_x = P \frac{\sqrt{p_{out}}}{d} \qquad (7)$$

According to Eq. (6), $\log(P)$ as a function of $1/T$ should present a straight line, the slope of which depends on the activation energy of the process. The results obtained for the clean membrane and covered with a layer of palladium are shown in Fig. 2.

Using the least squares method, we determined the slope of the corresponding straight lines and consequently activation energy values which are shown in Fig. 3.
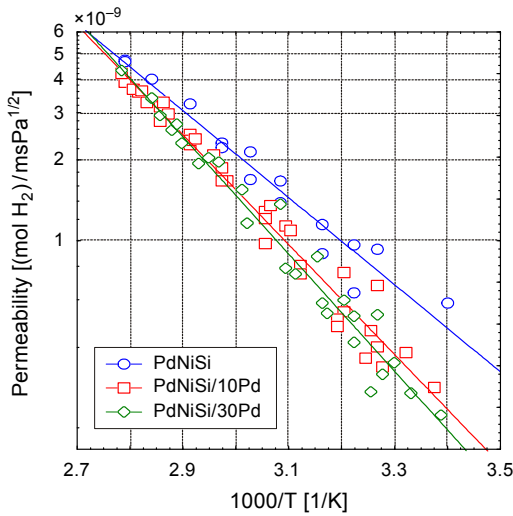

Fig. 2. Arrhenius plots of the hydrogen permeability of the samples prepared in this study.
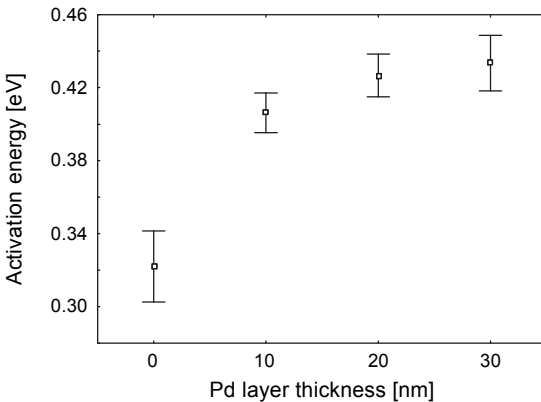

Fig. 3. The activation energy of the hydrogen permeation as a function of the thickness of the Pd layer.

It may be noted that the activation energy of hydrogen permeation through the amorphous membrane $Pd_{33}Ni_{52}Si_{15}$ is greatly increased when the membrane is coated with Pd. Within the limits of measurements uncertainty, it can be assumed that it does not depend on the thickness of the vapour deposited palladium and is (0.42 ± 0.01) eV. For comparison, the activation energy of the process for a pure palladium membrane is 0.23 eV [8].

Basing on these data, the potential barrier for the hydrogen permeation through the membrane uncoated and coated with palladium can be schematically drawn. However, to do this, it is necessary to determine the energy that causes the hydrogen permeation through the membrane. From a thermodynamic point of view, the driving force of penetration is a thermodynamic force [9] which represents the spontaneous tendency of hydrogen molecules to the energy dissipation resulting from the second law of thermodynamics and the tendency of the system to maximize entropy. When the hydrogen passes in constant pressure and temperature through an area where there is a gradient of chemical potential μ, this force can be written as

$$F = -\frac{\partial \mu}{\partial x} \tag{8}$$

so the work which has to be done during hydrogen permeation is

$$dw = -F dx \tag{9}$$

In our experiment, the values of thermodynamic forces can be only estimated. Assuming that we are dealing with an ideal solution in which concentration of hydrogen in the membrane decreases exponentially with the thickness and that we know the decay constant of this concentration, it can be shown that the amount of work done during penetration in the studied temperatures is of the order of 10^{-3} eV and may be omitted in simplified models of existing barriers. Figure 4 shows a schematic model of the potential existing for the test membrane during the hydrogen permeation.
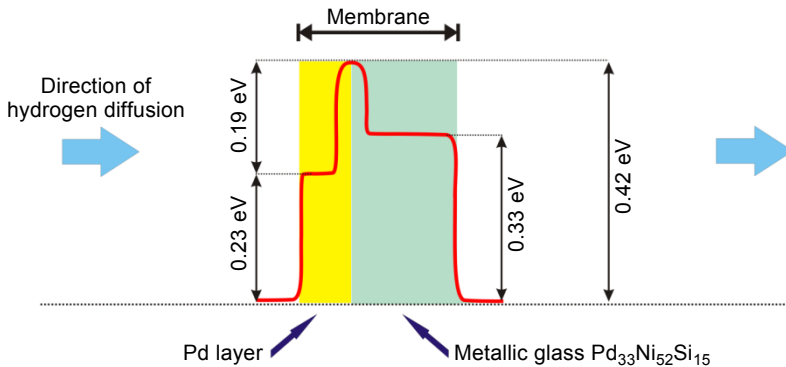

Fig. 4. Simplified potential energy diagram of the Pd/PdNiSi membrane.

So there is a potential barrier at the palladium–metallic glass interface with value (0.190 ± 0.009) eV. Simultaneously, almost two-fold reduction in the hydrogen permeate is observed [10]. It can be concluded that the increased amount of palladium on the metallic glass surface reduces the efficiency of diffusion of hydrogen. Binding energies of hydrogen with palladium and nickel surfaces are similar, and are from 260 to 267 kJ/mol and from 261 to 264 kJ/mol, respectively (depending on the crystal plane) [11]. However, the initial sticking probabilities s_0 for hydrogen on metal surfaces for dissociative adsorption are: 0.5 to 0.7 for Pd and 0.06 to 0.01 for Ni [11]. According to Eqs. (3), (5) and (8) the more of palladium on the surface, the greater concentration of hydrogen and greater thermodynamic force, and thus the larger flow of permeate hydrogen. However, in the case of a vapour-deposited layer of Pd this effect is offset by an increase of potential barrier on the interface between palladium–metallic glass. On the palladium–glass boundary, hydrogen is observed to be in the state characteristic for solid solution, different from this observed due to absorption on the surface. Since heat of H dissolution in Ni is +16 kJ/(mol H) [12], H atoms do not spontaneously dissolve in Ni metal, whereas for Pd it is –10 kJ/(mol H), resulting in spontaneous dissolution of H in Pd metal. Moreover, the hydrogen solubility in Pd is approximately 100 times larger than that in Ni. Hydrogen diffusion in Pd is also much faster than in Ni. The vapour-deposited palladium layer, formed on the nickel surface, caused at the interface the potential barrier for hydrogen permeability of a value 0.26 eV. Since the metallic glass test contains 33% of palladium, it can be assumed that form membranes with palladium layers the potential barrier will be proportionately reduced to about 0.18 eV. As shown in Fig. 3 the determined potential barrier height for hydrogen permeability at the palladium–glass interface is (0.190 ± 0.009) eV, which is fully in line with the proposed model.

4. Conclusions

In this paper, the results of investigation into the influence of thin layers of palladium created on the surface of the amorphous alloy $Pd_{33}Ni_{52}Si_{15}$ on the hydrogen permeation were presented. These results showed that, contrary to our expectations, the quantity of the permeating hydrogen flux decreases with an increase of Pd layer thickness, and for such membranes, the activation energy for the hydrogen permeation process increases almost twice, as compared to the pure Pd membrane. It appears that the process of hydrogen permeation through the membrane is very important for a multi-value heat of dissolution of hydrogen in the individual layers. The difference in these values is responsible for the changes in the value of the activation energy of the process.

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