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Electrical conductivity of $Pd_{47}Ni_{47}Si_6$ amorphous membrane while hydrogen permeation*

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Hydrogen diffusion through an amorphous membrane causes local disorders in the structure which can be detected through the measurement of changes of the electrical conductivity. Detecting these changes and comparing them directly with the amount of the permeated hydrogen provides information on the efficiency of separation, which can be used in hydrogen sensor and analyzer technology. This paper presents the results of electrical resistivity measurement of $Pd_{47}Ni_{47}Si_6$ alloy amorphous membrane while hydrogen permeation flux was being changed along with the temperature. It was found that hydrogen changes the nature of the resistivity and the temperature coefficient of resistivity is negative, however, starting from the temperature of 365 K, its value becomes smaller. In order to explain this phenomenon thorough and detailed measurements of phase transitions were made with the use of differential scanning calorimetry and X-ray diffractometry. On the basis of the research an attempt was made to explain the recorded changes of electrical conductivity.

Keywords: *hydrogen separation; amorphous alloys; palladium-based alloy; electrical conductivity*

1. Introduction

Hydrogen interaction with amorphous alloys has been studied extensively due to both scientific and technological interest. In the framework of a more comprehensive investigation of hydrogen interaction with amorphous alloys, simple methods monitoring efficiency of hydrogen separation are searched for. One of the results of the process of hydrogen permeation through a membrane of an amorphous structure is changing its electrical conductivity. Connecting these changes with the amount of the permeate hydrogen could make it possible to monitor and control the diffusion process efficiency [1]. Such system could also work as a hydrogen sensor in the devices using fuel cells. The paper presents the results of electrical resistivity measurement of a membrane made of amorphous $Pd_{47}Ni_{47}Si_6$ alloy while the permeate hydrogen was being affected by changing the temperature. The alloy demonstrated high hydrogen selectivity and permeability, which proved it to be a very good material for membranes used for separation. The registered changes in the electrical resistivity in the adopted experimental conditions made it possible to simultaneously combine in the membrane the function of a separator and a hydrogen analyzer.

2. Experimental

The study used $Pd_{47}Ni_{47}Si_6$ amorphous alloy which was obtained by a melt spinning method in the form of a tape which was 25 mm in width and 50 μm in thickness. The amorphicity of the alloy was examined with the use of X-ray diffractometry (CuK_α, 40 kV, 30 mA, hereafter denoted as XRD) while the alloy composition was examined with the use of an X-ray EDX microanalyser. Thermal stability of the amorphous phase was examined by differential scanning calorimetry (hereafter denoted as DSC) at a heating rate of 0.5 K/s.

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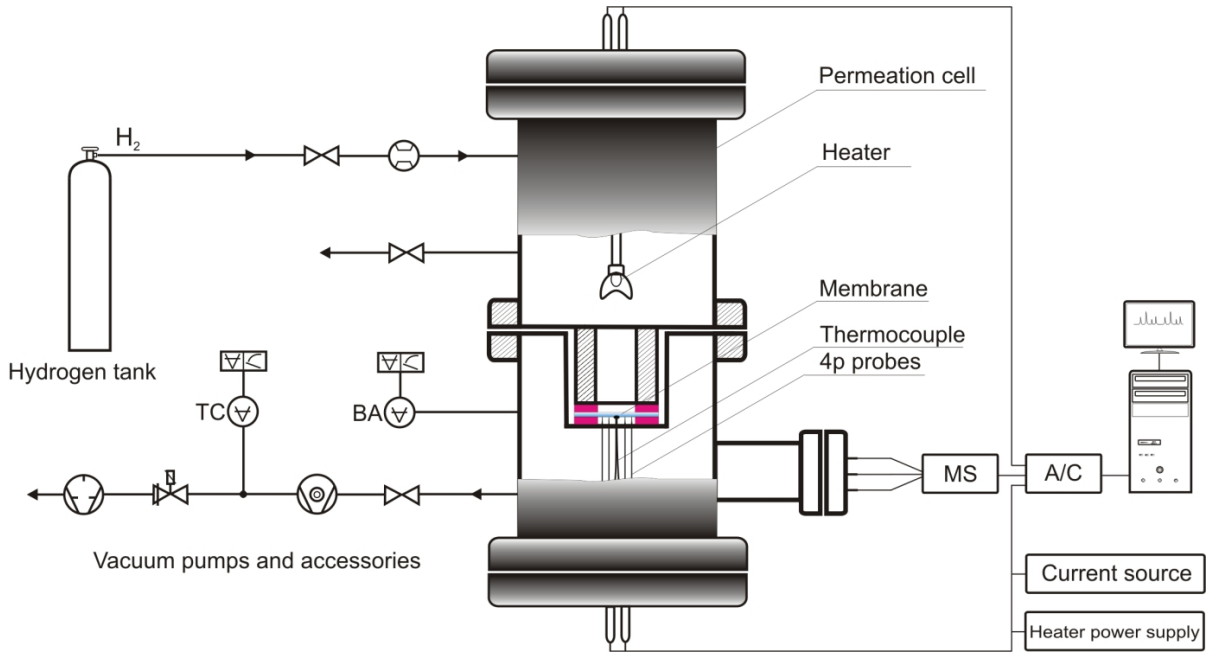

Fig. 1. The schematic diagram of a permeation test apparatus.

A disc with the diameter of 24 mm was cut out from the tape and was placed in the test chamber. In the research investigating electrical resistivity during hydrogen permeation through the membrane the four-probe method was used, which is one of the most common methods of measuring electrical resistivity of solids. The measurements were carried out using a probe with four linearly positioned, evenly distanced blades which were attached to the sample from the side of the vacuum chamber. The measurements were made with the use of the Keithley SourceMeter2400 instrument. The diagram of the permeation test apparatus is shown in Fig. 1.

In the measuring chamber the initial total pressure was 1×10^{-6} Pa. The hydrogen permeation was measured by a conventional gas-permeation technique [2, 3] using pure hydrogen gas in the temperature range of 293 – 350 K under the hydrogen pressure equal to 102 kPa. The partial pressure of the hydrogen was measured with the use of RGA100 Stanford Research System mass spectrometer and the membrane temperature was determined with a NiCr–Ni thermocouple.

3. Results and discussion

Fig. 2. shows the recorded changes in the resistivity with temperature in a vacuum and in the presence of hydrogen permeating through the membrane. The resistivity of the amorphous membrane in a vacuum increases linearly. However, at temperatures of 345 K and 365 K a discontinuity of these changes can be observed. Up to the temperature of 345 K, the temperature coefficient of resistance was $(2.67 \pm 0.06) \times 10^{-3}$ 1/K. Subsequently, for the temperature of 365 K it was $(1.32 \pm 0.12) \times 10^{-3}$ 1/K, and above that temperature it was $(1.44 \pm 0.03) \times 10^{-3}$ 1/K. Hence, at these temperatures phase transitions in the amorphous structure were expected to occur. In order to confirm this hypothesis, an X-ray phase analysis was performed for the $Pd_{47}Ni_{47}Si_6$ alloy membrane directly after the synthesis (as quenching) at 300 K temperature. Next, an X-ray phase analysis was carried out while annealing the membrane at the temperature of 380 K, and then again after cooling the membrane down to the temperature of 300 K. The results are shown in Fig. 3. The registered diffraction patterns

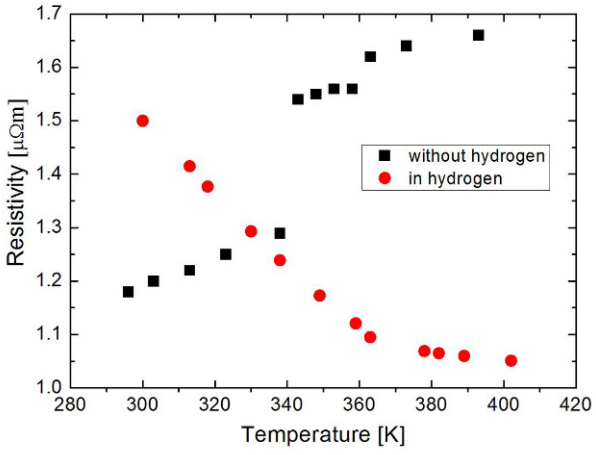

Fig. 2. Temperature dependence of electrical resistivity of $Pd_{47}Ni_{47}Si_6$ alloy in the vacuum and in the presence of hydrogen.

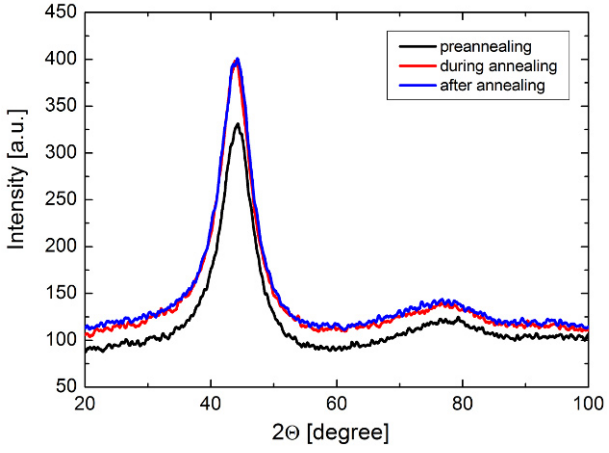

Fig. 3. XRD pattern of the $Pd_{47}Ni_{47}Si_6$ amorphous membrane.

clearly show that the membrane material has an amorphous structure. After heating the membrane to the temperature of 380 K only an increase of the background is observed, which could be caused by an increase in the thermal disorder in the sample surface. To explain the abrupt changes in the resistivity, measurements of the structure stability were also made with the use of differential scanning calorimetry (DSC). The obtained DSC curve is shown in Fig. 4. At 345.5 K there occurs a small exothermic peak which is indicative of the formation of the crystalline phase. However, because there are no such changes in the diffraction patterns, it can be assumed that these are structural

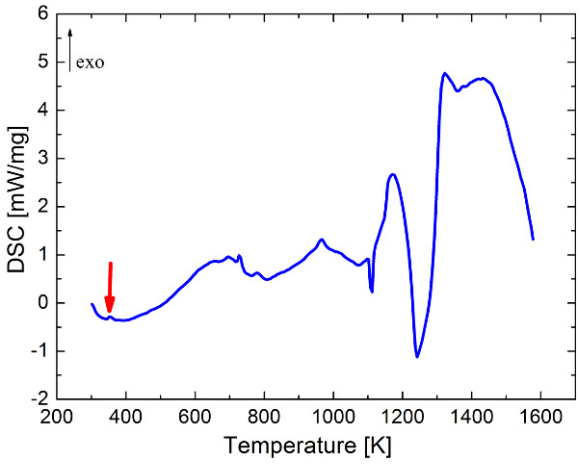

Fig. 4. Differential scanning calorimetry of the $Pd_{47}Ni_{47}Si_6$ amorphous membrane.

relaxations of microvoids resulting in changes in the mobility of electrons involved in the electrical resistivity [4, 5]. Unfortunately, the second step of the resistance change at 365 K, (Fig. 2) is not reflected on the registered calorimetric curve. Up to the temperature of 720 K no other changes in the structure have been observed.

The hydrogen permeation through the membrane when its temperature increases, results in a drastic change in the electrical resistivity, as shown in the graph in Fig. 2. The temperature coefficient of resistance is negative and until the temperature reaches the value of 365 K it is $(6.53 \pm 0.14) \times 10^{-3}$ 1/K, and above this temperature it is $(1.11 \pm 0.18) \times 10^{-3}$ 1/K. It is usually observed that an increase in the resistance of an amorphous alloy goes together with an increase in hydrogen concentration [6–8]. However, in some cases at low concentrations of hydrogen in the alloy, the process can be reversed [9]. According to the Matthiessen rule, the resistivity of a perfectly pure metal and the resistivity caused by impurities and defects are additive values which in total give the final total resistivity:

$$\rho = \rho_{phonons} + \rho_{imp} + \rho_{defects}. \qquad (1)$$

The electrical resistivity of amorphous structures results from extended energy states and is highly limited by diffusion processes associated with

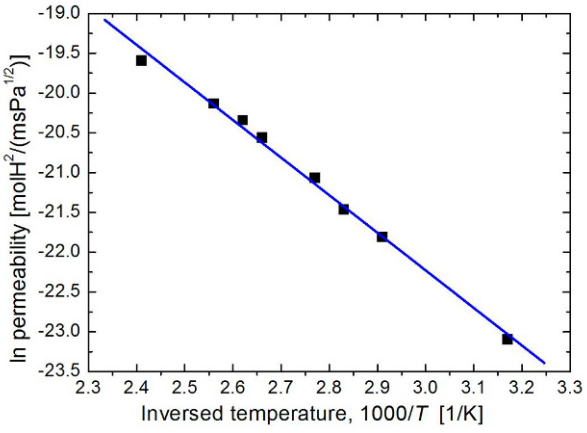

Fig. 5. Arrhenius plot of hydrogen permeation for $Pd_{47}Ni_{47}Si_6$ glassy alloy.

the disordered structure. Since there is static structural disorder in metallic glass, then the change in resistance primarily results from an increase of the defects caused by the diffusion of hydrogen. For this reason, the temperature coefficient of resistivity of the metallic glass is lower than for crystalline alloys. However, in the case of $Pd_{47}Ni_{47}Si_6$ alloy the resistivity decreases when the temperature increases, which means that the diffusible hydrogen does not cause significant changes in the structure. The influence of separation temperature on hydrogen permeation flux of the membrane is shown in Fig. 5. The curve in the graph is a straight line, therefore the size of the flux of permeating hydrogen fulfills Sievert's law [10]. From this Arrhenius plot, apparent activation energy of (0.40 ± 0.01) eV for hydrogen permeation across the membrane was estimated. For comparison, the value of the activation energy for pure palladium is 0.23 eV [11]. During adsorption on the surface of a metallic alloy, molecular hydrogen dissociates to atoms, and then creates an electropositive phase β^+ giving away an electron, which, as the diffusible hydrogen flux increases, raises the concentration of conduction electrons and reduces the residual resistance. Diffusing hydrogen can, however, change the resistance of the membrane in other ways. Firstly, interstitial hydrogen increases local disturbance in the crystal lattice by increasing the distances between close atom neighbours in short-range order. Secondly, additives usually modify the electronic structure, thus changing the energy of Fermi, density of states and effective mass of electrons. Moreover, hydrogen affects the elastic constants of the lattice itself by modifying the phonon spectrum responsible for the electron-phonon scattering. All of these factors may change the value of resistance of the alloy and are associated with the formation of hydride phase in the metal alloy. Both Pd, Ni and Si form stable compounds with hydrogen [12]. Thus there is high probability that hydrogen can also create a stable bond in the alloy of these metals. Since the change in the resistivity of the alloy in the presence of permeated hydrogen shows an irregular change at the temperature of 365 K, this may suggest that it is connected with the transition of the alloy from phase α to phase β. The experiment was conducted at a relatively low hydrogen pressure, which resulted in a small amount of hydrogen in the α phase in the alloy [13]. This led to the generation of local states of hydride which altered the number of free electrons participating in the electrical conductivity. This is consistent with the theoretical calculations of electron density of states for palladium and palladium hydride presented in the paper [14]. Hence, the thesis that a change in temperature coefficient of resistivity at 365 K results from the local states of metal hydride, is highly probable.

4. Conclusions

Synthesized $Pd_{47}Ni_{47}Si_6$ metallic glass is a good material for membranes for selective separation of hydrogen. The resistance of the alloy increases linearly with the temperature, increasing up to 345 K with the temperature coefficient $(2.67 \pm 0.06) \times 10^{-3}$ 1/K, then to a temperature of 365 K with the temperature coefficient being $(1.32 \pm 0.12) \times 10^{-3}$ 1/K, and above this temperature with the temperature coefficient of $(1.44 \pm 0.03) \times 10^{-3}$ 1/K. During the diffusion of hydrogen a change of the sign of the temperature coefficient of resistance to negative is observed, i.e. up to the temperature of 365 K

it is (6.53 ± 0.14) × 10^{-3} 1/K, and above this temperature it is (1.11 ± 0.18) × 10^{-3} 1/K. It was found that the structural relaxation of microvoids occurring at 345 K does not influence the process of hydrogen permeation. It was confirmed that there is a relationship between changes in the resistance of $Pd_{47}Ni_{47}Si_6$ alloy and the thermally activated size of hydrogen streams permeating through the membrane.

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