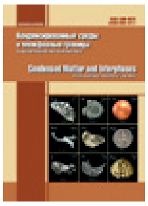

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The effect of the chemical compositions of palladium alloys on their hydrogen permeability

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Abstract

The purpose of the article is to identify the effect of the alloying element in palladium alloys on their parameters of hydrogen permeability.

Cyclic voltammetry and anodic-cathodic chronoamperometry were used to study the electrochemical behavior of cold-rolled alloys of Pd-5Pb, Pd-6Ru, and Pd-7Y systems (wt. %) in the processes of atomic hydrogen injection and extraction in a deaerated aqueous solution of 0.1 M H_2SO_4.

The study identified the role of lead, ruthenium, and yttrium in the processes of atomic hydrogen injection and ionization. Voltammetry and chronoamperometry data indicate a higher ionization rate for the Pd-6Ru alloy. The parameters of hydrogen permeability calculated from the cathodic current drops show that the hydrogen permeability of alloys varies in the series: Pd-6Ru > Pd-7Y > Pd-5Pb. The effective constant of the injection rate coincides for all alloys within the measurement error, whereas the effective constant of the extraction rate of atomic hydrogen is higher for Pd–5Pb. The marginal solubility of ruthenium in the Pd-6Ru alloy contributes to the passivation of grain boundaries in the alloy with excess ruthenium. As a result, there is preferential movement of hydrogen solely along the grain body. This results in higher hydrogen permeability.

Keywords: palladium, Pd-7Y, Pd-5Pb, Pd-6Ru alloys, hydrogen permeability, atomic hydrogen, phase-boundary transition, membrane separation

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1. Introduction

Hydrogen is now seen as a key component of clean energy production, i.e. a 21st century energy solution and a post-oil era fuel. It is expected to mitigate the threat of global warming, while ensuring the sustainable and environmentally friendly energy production. Hydrogen can be produced by various methods, such as water-gas transition, fossil fuel reforming, and water electrolysis [1–3]. However, hydrogen produced by these methods normally contains gaseous impurities that need to be further separated. Membrane separation is viewed as a promising technology for the production of high-purity hydrogen due to its efficiency, energy conservation, ease of operation, and environmental friendliness [4–6].

Palladium has high selectivity to hydrogen and permeability, plasticity, and high chemical compatibility [7, 8]. Its alloys are widely used as membrane materials in hydrogen separation technologies, which reduces its production expenses [9]. The composition of the alloy has a significant impact on its permeability to hydrogen. Metal membranes can contain metals and alloys with a number of elemental components that limit the diffusion of the H atom through the alloy membrane [10, 11]. What is more, the high cost of palladium is a major limitation for its application in industry. Therefore, alternative alloy membranes with higher hydrogen permeability, lower cost, and richer resources than Pd alloy membranes are needed.

Doping palladium with such chemical elements as Pb, Ru, Cu, Y, and Ag can increase the service life of the membrane [12–14]. In addition, even small amounts of some metals lead to increased hardness, durability, and corrosion resistance and facilitate the H sorption and desorption processes.

Fusion of Pd and Ru is a promising method for producing Pd-metal alloy membranes with satisfactory characteristics and durability [15]. The mechanical, physical, electrical, kinetic, and thermodynamic properties of the PdRu system have been studied for a long time [16].

The Pd-Ru system exhibits limited solubility over the entire range of compositions and temperatures. The solubility of Ru in Pd increases with an increase in temperature and reaches its maximum value at the peritectic temperature for a sample containing 21% of Ru. In [17], it was reported that the hardness of the Pd–Ru alloy membrane is 80% higher than that of pure palladium, while its permeability to hydrogen is very close to pure palladium in the range of 4.5–10 wt. % Ru. Consequently, Pd-Ru alloys with a homogeneous structure and an arbitrary metal ratio are of high interest for fundamental research projects and commercial design of materials [18].

Pd-Y alloy membranes can be used for the purification of H from impurities. Many papers [19–21] have shown that these alloys have a higher diffusion permeability than pure palladium. Adding just 1.68 at. % of Y increases hydrogen permeability at 300 °C by about 80% as compared to pure Pd, while the addition of ~ 8 at. % of Y increases permeability by more than 5 times [22]. The Pd-8Y membrane exhibits the maximum permeability observed over the measured temperature range of 25 to 460 °C. However, according to [21], when palladium is doped with yttrium, the Pd_7Y phase is formed, which reduces the solubility and diffusion of hydrogen. Therefore, it is most advisable to use alloys with a low atomic fraction $X_Y \leqslant 0.06$.

The Pd-Pb alloy is promising due to its high hydrogen permeability. Additions of lead considerably harden palladium with a slight reduction in plasticity and increase hydrogen permeability. The maximum solubility of lead in palladium is achieved at a eutectic temperature (1,470 K) and is 20 wt. % [23]. The maximum hydrogen permeability is characteristic of the alloy with 8 at. % of Pb [24].

This study was conducted on palladium alloys with yttrium, lead, and ruthenium. The purpose of the work was to identify the role of the alloying element in palladium alloys on the parameters of hydrogen permeability.

2. Experimental

This study was conducted on Pd-5Pb (95 wt. % of Pd and 5 wt. % of Pb), Pd-6Ru (94 wt. % of Pd and 6 wt. % of Ru), and Pd-7Y (93 wt. % of Pd and 7 wt. % of Y) alloys. All studied alloys were substitutional solid solutions with an FCC lattice. To obtain foil, the given alloys were subjected to cold rolling followed by annealing at 950 °C for

3 hours and then rolling on a four-high rolling mill in 10 passes with intermediate vacuum annealing at 900 °C for 30–90 min. The thickness of the studied samples was: *L*(Pd-5Pb) = 46 μm, *L*(Pd-6Ru) = 30 μm, and *L* (Pd-7Y) = 50 μm. The thickness was measured with an MCC 25 electron micrometer.

The geometric characteristics of the studied alloy surfaces were determined by atomic force microscopy (AFM) with a Solver P47PRO atomic force microscope in a semi-contact (intermittent-contact) scanning mode*.

The working solution in which the studies were conducted was a deaerated solution of 0.1 M H_2SO_4 (extra pure) prepared in bidistilled water. To deaerate the working solution, chemically pure argon was passed through the cell for 30 minutes.

When preparing the electrode for the experiment, the foil surface was cleaned, i.e. degreased with chemically pure ethanol and washed with distilled water. Then, a conductive graphite glue was used to deposit the foil on the graphite electrode. The area of the foil had been measured and did not exceed 0.5 cm^2. Each sample was used for one cycle of the experiment, which involved quadruple potential cycling and obtaining a series of chronoamperograms for different hydrogenation time from 1 to 10 s. After one cycle, the sample was replaced.

Electrochemical measurements were conducted in a glass three-electrode cell at a temperature of 25 °C using a copper sulfate reference electrode (0.311 V). Platinated platinum Pt(Pt) was used as an auxiliary electrode. Spectrally pure graphite electrode was used as a working electrode onto which thin samples of metal foil were deposited with a conductive graphite glue.

The measurements were taken using a computer-aided IPC-Compact potentiostat. All potentials were recalculated relative to a standard hydrogen electrode and the current values were given per single unit of the visible surface.

The studied electrode was placed in an electrochemical cell filled with a working solution, kept for 500 seconds at a pretreatment potential E_{pp} (for surface cleaning), the value of which was 0.3 V.

The cyclic voltammograms were obtained at a potential scan rate of 5 mV/s, starting from E_{pp} to the cathodic region until the appearance of a noticeable cathodic current of hydrogen reduction (E = -0.14 V). Then, the potential sweep was switched to the anodic region until oxygen was released (up to E = 1.5 V). Cycling was carried out 4 times in the same potential range for electrochemical cleaning of the electrode surface and its standardization.

Chronamperograms were recorded immediately after the voltamperograms were obtained. During the first step, the electrode surface was standardized for 500 s at the potential E_{pp}. Step 2 involved injecting atomic hydrogen at a hydrogenation potential of -0.14 V. During each cycle of obtaining chronamperograms, the hydrogenation time was changed from 1 to 10 s. During the third step, atomic hydrogen was extracted from the alloy at the peak ionization potential. The ionization potential was determined from the data of the previous voltammograms, i.e. the fourth cycle, and could change when the foil sample was replaced.

3. Results and discussion

3.1. Examination of the foil surface relief

Characteristics of Pd and its alloys and roughness according to the results of AFM studies are given in Table 1.

The analysis of the data in Table 1 showed that the surface roughness of all studied alloys was almost the same (Fig. 1) and there was little difference between the parameters of their crystal lattices. The main difference in the nature of the second component was connected with their electronic structure. Ruthenium and yttrium are *d*-metals that exhibit good solubility in relation to hydrogen. However, Pb is a *p*-metal, for which this property is not characteristic. Therefore, it can be assumed that the Pd-Pb alloy may exhibit lower hydrogen permeability as compared to Pd-Ru and Pd-Y.

The limited solubility of ruthenium in palladium [25] caused a release of excess Ru along the boundaries of the crystal lattice of the studied alloy. This led to the passivation of the intercrystalline space, which prevented the movement of atomic hydrogen along the boundaries in the alloy [26]. As established in

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* The research was carried out using the equipment of the Center for Collective Use of Scientific Equipment of Voronezh State University.

Table 1. Characteristics of palladium and its alloys

ω(X), wt. %	Pd	PdX		
		5Pb	6Ru	7Y
Electronic configuration	[Kr] $4d^{10}5s^0$	[Xe] $4f^15d^16s^26p^2$	[Kr] $4d5s^1$	[Kr] $4d^15s^2$
Atomic radius r, pm	137	175	134	178
Lattice parameter [23], nm	0.3890	0.3908	0.3879	0.3875
Roughness, nm (30×30 μm^2)	–	34±5	33±5	32±5

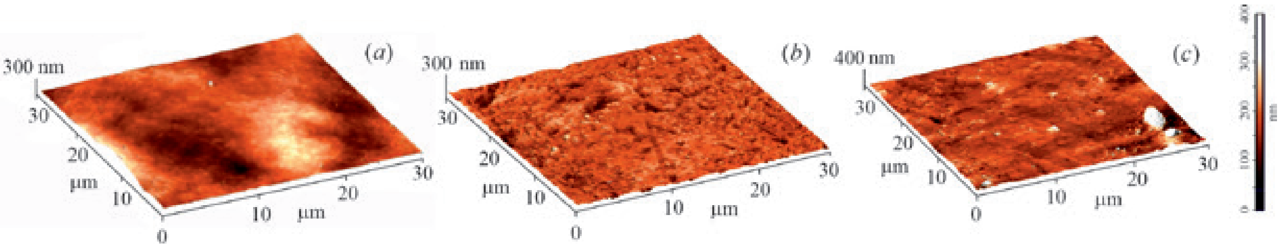

Fig. 1. AFM micrographs of the surface of the Pd5Pb (a), Pd6Ru (b), and Pd7Y (c) alloys

[27], the flow of atomic hydrogen through the crystallite body is dominant and it induces the appearance of various structural defects.

3.2. Electrochemical research

Cyclic voltammograms obtained for all studied alloys were similar. For Pd-6Ru and Pd-5Pb alloys, at a potential of about 0.5 V from the first cycle of voltammograms, there was a clearly expressed anodic peak related to the ionization of atomic hydrogen (Fig. 2a, 3a). At a potential of about 0.7 V, there was a small peak corresponding to the reduction of palladium oxide. The PdO was formed on the anodic branch of the curve in the range of potentials from 1.2 to 1.3 V and could be observed in the form of a subtle current peak. This fact is confirmed by previous studies [28], as well as the constant position and height of the PdO reduction peak for all studied alloys.

Together with Pd oxidation at a potential of about 1.2 V, there was a pronounced anodic peak for the Pd-7Y alloy, which decreased during the transition from cycle 1 to cycle 4 (Fig. 4a). We explained this peak by the electrooxidation of annealing artifacts of organic substances used during rolling of the alloy to produce foil.

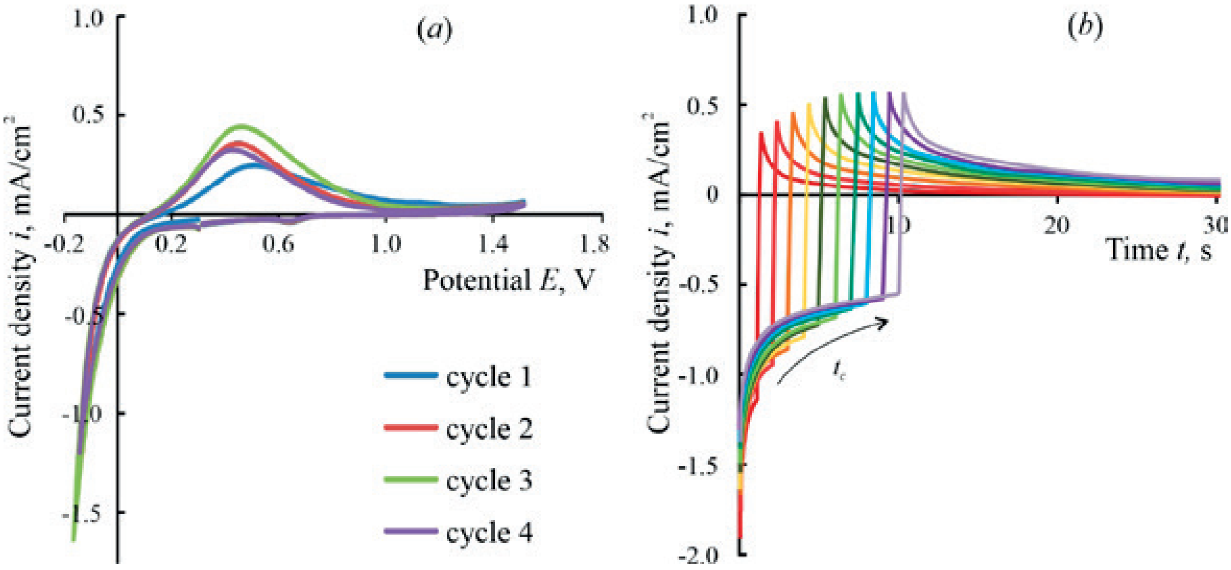

Fig. 2. Cyclic voltamperograms (a) and chronoamperograms (b) of the Pd-5Pb foil in 0.1 M H_2SO_4

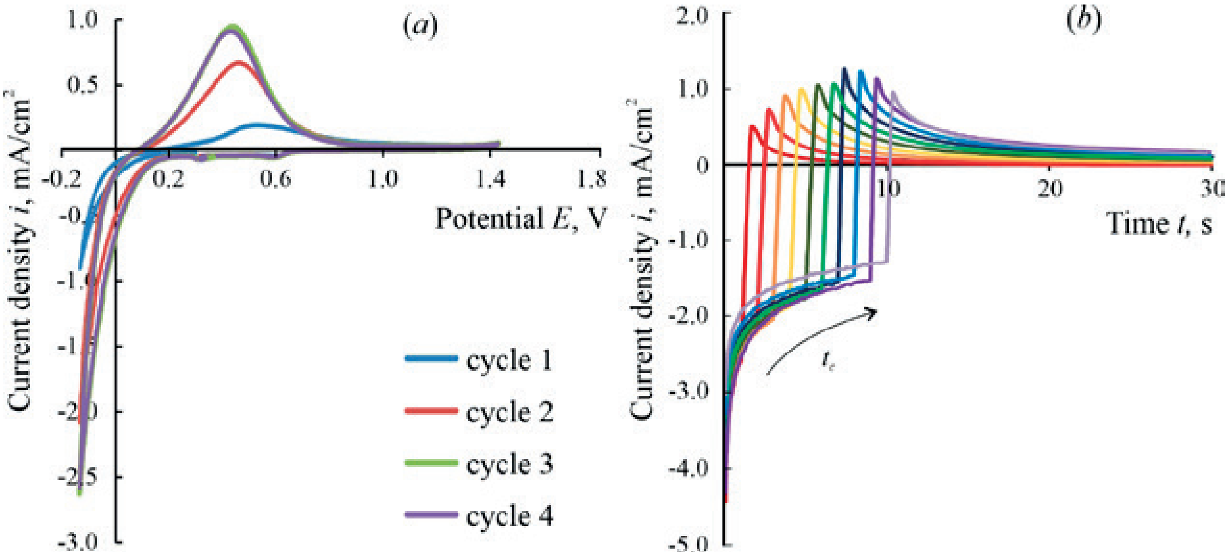

Fig. 3. Cyclic voltamperograms (a) and chronoamperograms (b) of Pd-6Ru foil in 0.1 M H_2SO_4 of the studied sample

Interestingly, during the first cycle of the Pd-7Y voltammogram, there was no peak of hydrogen ionization, however, it developed gradually during further cycling of the potential. This occurred simultaneously with the disappearance of the electrooxidation peak. Most likely, this was due to blocking of active adsorption centers that prevented the interaction of atomic hydrogen with the alloy surface.

The height of the peak of hydrogen ionization on Pd-5Pb and Pd-7Y alloys reached 0.5 V, while on Pd-6Ru alloy it was almost twice as high. Quadruple potential cycling contributed to the cleaning of the alloy surface, which resulted in the growth of peak of atomic hydrogen ionization [29].

Cathodic i,t-curves for all alloys were characterized by a sharp decline (Fig. 2b-4b). With an increase in the hydrogenation time from 1 to 10 s, there was a decrease in cathodic chronoamperograms. The maximums of the cathodic curves corresponding to the zero degree of surface covering decreased by 1.5 times with an increase in t_c, and this applied to all alloys. The injection rate of atomic hydrogen, which is characterized by the cathodic current, was lower for the Pd-5Pb alloy than for other alloys.

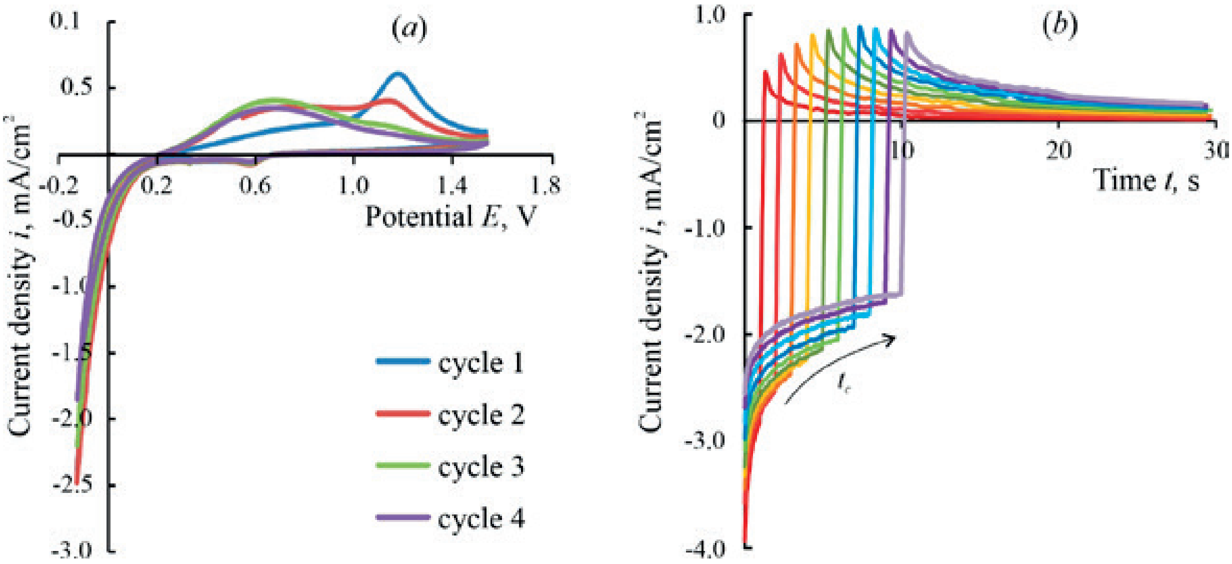

Fig. 4. Cyclic voltamperograms (a) and chronoamperograms (b) of Pd-7Y foil in 0.1 M H_2SO_4 of the studied sample

The anodic chronoamperograms corresponding to H extraction was increasing with an increase in hydrogenation time during the first few seconds and then the value remained almost constant. For the Pd-6Ru alloy, the value of the injection rate was higher (Fig. 3b). The nature of the decline of the anodic *i,t*-curves was similar for all alloys. This fact can be used as a proof that the kinetics of the injection-extraction processes of atomic hydrogen are invariable.

3.3. Calculating the parameters of hydrogen permeability

The nature of the second component in the processes of atomic hydrogen injection and extraction can be conveniently identified when comparing the parameters of their hydrogen permeability. A mathematical model describing the injection and extraction of atomic hydrogen in alloys of semi-infinite thickness (L > 10 μm) was used to calculate these parameters [30].

According to the theoretical modeling of the process of injecting atomic hydrogen for compact electrodes, the total cathodic current drop at the initial stage ($t \leqslant 3$ s) can be described by equation (1):

$$i_c(t) = i_c(0) - F\overleftarrow{k}\left[c^s_{\bar{\mathrm{H}}}(\eta_c) - c^e_{\bar{\mathrm{H}}}\right]\frac{2\overleftarrow{k}t^{1/2}}{\pi^{1/2}D_{\mathrm{H}}^{\;1/2}} = \\ = i_c(0) - \left[i_c(0) - i_c^{\infty}\right]\frac{2\overleftarrow{k}}{\pi^{1/2}D_{\mathrm{H}}^{\;1/2}}t^{1/2}, \qquad (1)$$

where $i_c(0)$ and i_c^{∞} are the initial and stationary cathodic current of the chronamperograms, respectively; $\overleftarrow{k}$ is the effective constant of the extraction rate of atomic hydrogen; and D_{H} is the diffusion coefficient of H in the metallic phase.

At the time of the cathodic chronamperogram $t > 4$ s, the limiting stage from the phase boundary transition is passed to the stage of solid-phase diffusion of hydrogen in the alloy and can be described by the equation:

$$i_c(t) = i_c^{\infty} + \frac{FK_{\mathrm{D}}}{\pi^{1/2}}t^{-1/2}. \qquad (2)$$

Based on (2), it is possible to find the hydrogen permeability coefficient, K_{D}, which includes the solid-phase diffusion coefficient of H and the change in the concentration of hydrogen in the foil relative to its equilibrium value $\Delta c_{\bar{\mathrm{H}}} = c^{\mathrm{s}}_{\bar{\mathrm{H}}}(\eta_c) - c^{\mathrm{e}}_{\bar{\mathrm{H}}}$:

$$K_D = \Delta c_{\mathrm{H}} \cdot D_{\mathrm{H}}^{1/2}. \qquad (3)$$

The analysis of the cathodic current drops corresponding to the hydrogenation time of 10 s allowed obtaining hydrogen permeability coefficient K_{D}, the effective constants of the injection and extraction rates of atomic hydrogen $\vec{k}$, and $\overleftarrow{k}$, respectively, and the effective constant of phase boundary equilibrium $K = \vec{k}/\overleftarrow{k}$. Also, the concentration of atomic hydrogen in the Δc_{H} alloy was estimated from (3) under the assumption that the alloys are enriched with palladium and there is little difference between diffusion coefficients of atomic hydrogen in them and pure Pd.

The obtained values of the hydrogenation parameters obtained from the cathodic current drops are given in Table 2.

The hydrogen permeability K_D and, as a consequence, the concentration of atomic hydrogen in the Δc_{H} alloy increased in the Pb→Y→Ru series. The large values of the confidence intervals for all obtained parameters can be explained by the fact that different foil sections of the same alloy were studied, which could differ slightly in their structure and roughness.

The values of the effective constants of injection $\vec{k}$ and extraction rates $\overleftarrow{k}$ differ slightly and coincide within the limits of experimental error. However, the atomic hydrogen transition through the solution/alloy interphase was facilitated for Pd-6Ru alloy and inhibited for Pd-7Y alloy. What is more, the transition of

Table 2. Parameters of hydrogen permeability of the studied alloys, calculated from the cathodic current decays of chronoamperograms

Alloy	i_c^0, mA/cm^2	i_c^{∞}, mA/cm^2	$K_D \cdot 10^8$, mol/(cm^2·s$^{1/2}$)	$K \cdot 10^{-4}$, cm^{-1}	$\vec{k}$, s^{-1}	$\overleftarrow{k} \cdot 10^4$, cm/s	$\Delta c_{\mathrm{H}} \cdot 10^5$, mol/cm^3
Pd-5Pb	1.79±0.20	0.65±0.38	1.51±0.61	1.92±0.77	8.33±1.16	4.52±1.23	2.75±1.11
Pd-7Y	2.31±0.44	1.23±0.15	1.74±0.65	2.22±0.83	7.85±3.07	3.55±0.25	3.17±1.18
Pd-6Ru	2.43±0.23	1.12±0.31	2.08±0.46	3.32±1.73	9.60±2.78	3.63±0.89	3.80±0.83

atomic hydrogen from the alloy to the surface phase was easier for Pd-5Pb. The nature of the change in the phase boundary exchange constant was similar to that of the hydrogen permeability coefficient.

In previous research [31], it was established that the parameters of hydrogen permeability obtained from cathodic current drops are more informative and exclude the possibility of dilatation of the crystal lattice or hydrogen capture in octahedral and tetrahedral voids of the alloy [27, 32].

To sum up the obtained results, it can be concluded that the best hydrogen permeability is characteristic of the Pd-6Ru alloy as evidenced by the maximum values of the diffusion parameters K_D and Δc_{H}. This is probably due to similar values of the Pd and Ru atomic radii and the electronic structure that contributes to the dissolution of atomic hydrogen. There is little dependency of the kinetic parameters of injection and extraction on the chemical nature of the second component. For the Pd-7Y alloy, the formation of the intermetallic compound of Pd_7Y contributes to a decrease in hydrogen permeability [21]. In the case of Pd-5Pb alloy, the lowest hydrogen permeability values are most likely due to the electronic structure of lead, which is a *p*-element and has a filled 5*d*-sublevel. Also, fusion of Pd and Pb can be accompanied by the transition of *d*-electrons from the electronic sublevel of palladium to the *p*-sublevel of lead. The values of hydrogen permeability for the studied alloys obtained by other methods [33–35] are consistent in order and sequence of changes in values. However, an accurate comparison is impossible due to the different conditions of the experiments.

4. Conclusions

1. Palladium-based alloys with ruthenium, yttrium, and lead with nearly the same quantitative compositions have similar electrochemical behavior. The highest ionization rate of atomic hydrogen is characteristic of the Pd-6Ru alloy. Whereas surface contamination by annealing artefacts of organic substances used during rolling is most evident in the Pd-7Y alloy where a strong adhesion of organic substances to the surface of the alloy might take place. The data of cathodic and anodic chronoamperograms generally confirm the voltammetric behavior of the studied alloys.

2. The hydrogen permeability parameters calculated from the cathodic current drops show that the hydrogen permeability (mol/(cm^2·s$^{1/2}$)) of alloys varies in the series: Pd-6Ru ($2.08{\cdot}10^{-8}$) > Pd-7Y ($1.74{\cdot}10^{-8}$) > Pd-5Pb ($1.51{\cdot}10^{-8}$).

3. The effective constants of the injection rate for all alloys coincide within the measurement error, and the effective constants of the extraction rate (cm/s) vary in the series: Pd-5Pb ($4.52{\cdot}10^{-4}$) > Pd-6Ru ($3.63{\cdot}10^{-4}$) ≈ Pd-7Y ($3.55{\cdot}10^{-4}$). Therefore, the extraction rate of atomic hydrogen is determined by the nature of the alloying element. The mechanism of atomic hydrogen penetration through the interface into the metal phase is the same for all alloys.

4. The marginal solubility of ruthenium in the Pd-6Ru alloy contributes to the passivation of grain boundaries in the alloy with excess ruthenium. As a result, there is preferential movement of hydrogen solely along the grain body. This results in higher hydrogen permeability.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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