Characteristics of hydrogen sorption/desorption for palladium foil doped by yttrium

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Abstract. Kinetics of hydrogen adsorption and desorption for palladium-7% yttrium foil was studied using volume metrics measurements in oil free vacuum cell. Preliminary H₂ was purified by diffusion from Pd-Ru membrane. Plots of the rate and constant rate of H₂ adsorption/desorption versus temperature in interval 333-573 K were obtained. It was found that H₂ sorption is the thermal activated process. The values of amount of H₂ adsorbed, rate Ws, constant rate Ks and activation energy of sorption Ea,s of H₂ sorption differs for initial foil surface and surface with preadsorbed hydrogen, which inhibits the repeated sorption. Due to preadsorbed hydrogen Ks decreases in 1.5 times (333 K) and Ea,s for molecular form of hydrogen adsorption increases in two times. Kinetics characteristics of hydrogen desorption depend on duration of the expose PdY foil in H₂ at room temperature. Long saturation leads to sharply decrease of the hydrogen desorption rate and to some increase of activation energy of desorption varying from 56-68 and 85-108 kJ/mol for first and second kinetic order respectively. Isotherms of hydrogen adsorption were of anomalous shape and can be explained by the induced adsorption model. The results of isotherms analysis agree with kinetic data.

1. Introduction
Due to the rapid progress of the hydrogen power engineering and a number of science intensive technologies, the demand for high-purity hydrogen (99.9999 vol %) is increased abruptly. Such high-purity hydrogen can be prepared only by its separation from hydrogen-containing gas mixtures via hydrogen diffusion through palladium-alloy membranes. The facile permeation of hydrogen through palladium and palladium alloys suggests a number of applications in some chemical processes. Gryaznov V M pioneered works on hydrogen diffusion through thin-walled pure metal Pd membranes for catalytic applications started in 1970-72 [1,2]. One of the first review about palladium alloys for hydrogen diffusion membranes appeared in 1977 [3]. Now a wide spectrum of Pd alloys with good characteristics of hydrogen uptake, permeability and thermal stability was offered for H₂ diffusion application not only for obtaining high purity H₂ [4,5], but as membrane that can be incorporated into the design of efficient reactors for hydrogenation, dehydrogenation steam reforming reactions [6,7]. The alternative and not extremely expensive use of Pd-film or PdNPs/H₂ systems in sensors gives a good perspective too [8,9]. Commercial manufacturing the low-price high-purity hydrogen and industrial application of membrane in catalysis calls for the development of a high variety of high-performance membrane palladium-based alloys, which must exhibit a combination of membrane characteristics, such as the high both hydrogen permeability, strength, and plasticity, low temperature-concentration dilatation in hydrogen atmosphere, high-corrosion resistance and catalytic activity in various gas media. Among investigated palladium alloys Pd alloys the best characteristics showed the palladium-yttrium membrane with 7 wt.% Y (table 1). It can be seen that the hydrogen permeability
Pd-7 wt.% Y depending on temperature in 2.3 times greater P values of industrial alloys B1 and Pd-In-Ru. Alloy Pd-7%Y has a high strength and plasticity sufficient for the purpose of obtaining thin foils.

Table 1. Mechanical properties of palladium-based membrane alloys in the annealed state and specific hydrogen permeability (P) at different temperatures [5].

| Alloy (wt.%)          | Hardness Hv, Kg /mm² | Ultimate tensile strength σ, kg ·mm⁻² | Relative elongation δ, % | P, m³·mm⁻²·m⁻²·h⁻¹·MPa⁻⁰·⁵ |
|-----------------------|----------------------|----------------------------------------|--------------------------|----------------------------|
| 100% Pd               | 40                   | 30                                     | 28                       | 0.7 1.01 1.35 1.68         |
| 93% Pd–7%Y            | 172                  | 60                                     | 16                       | 3.1 4.13 5.18 5.7          |
| B1                    | 103                  | 44                                     | 24                       | – 1.2 1.33 1.75           |
| 93.5%Pd–6%In–0.5%Ru   | 114                  | 48                                     | 26                       | 0.85 1.2 1.7 2.2          |

*sample composition Pd – 15%Ag – 2.5%Au – 0.7%Pt – 0.7%Ru – 0.3%Al

Thus, the interaction of hydrogen with palladium (Pd) is a subject of interest due to the potentially important applications in the area of metallic membranes and catalytic membrane technologies.

The aim of this study was to explore and compare kinetic characteristics of hydrogen adsorption and desorption processes at the temperature range of 25-380°C with foil Pd–7%Y.

2. Experimental

2.1 Foil preparation and analyses

High-quality alloys, and hence quality of thin foils depends on the chemical purity of the source components, especially RE metals and ways of manufacturing of alloys and foils of them. We use palladium 99.95% and yttrium double distillation (99.983%). For preparation of leak-tight thin foil with 30 µm thickness the following melting and rolling technologies were used. Rolling billets were melted out in electric-arc furnace under protective atmosphere (vacuum or inert gas) on the copper water-cold bottom. Melting was performed utilizing the tungsten non-consumable electrode. Production process flow chart is shown below.

2.2. H₂ sorption/desorption measurements

A sample of 93% Pd–7% wt.Y rolled foil with 30 µm thickness and 312 cm² visual surface (from two sides) was cut from a larger piece and put in adsorptive Pyrex glass cell (0.014 L) divided from adsorption vacuum set by metallic valves. The residual pressure in the set was better than 10⁻⁶ mm Hg (oil pumping, three traps with liquid nitrogen). The cell was coupled with system of gases (argon and hydrogen passed throw PdRu membrane). The H₂ pressure in adsorptive volume with foil (0.0094 L) was controlled automatically by calibrated thermocouple gauge, placed in thermostat (20±1°C). The
temperature of the foil in the cell maintained with a precision ±2°C. When temperature was more than 20°C in calculation of amount of H\textsubscript{2} in gaseous faze (number of H\textsubscript{2} molecules N) the thermo effusion was taken into account by coefficient \(\alpha = \left(\frac{T_2}{T_1}\right)^{\frac{1}{2}}\), where \(T_1\) and \(T_2\) are 293 K and temperature in adsorption/desorption tests respectively. The relative error in definition \(N\textsubscript{adsH2}\) and \(N\textsubscript{desH2}\) was not above 7%. Kinetics sorption and desorption was studied in static mode at constant temperature \(T_2\). Isotherms of H\textsubscript{2} (ads) sorption were obtained using dynamic adsorption method of Kavtaradze when hydrogen was introducing throw calibrated capillary in adsorptive cell with slow rate. The deviation between introduced and measured H\textsubscript{2} quantity permit to calculate hydrogen sorption. The Knudsen regime of gas transfer throw capillary at different input gas pressure was checked with argon.

2.3 Foil treatment and analysis

A sample of 93% Pd–7% wt.Y was outgassed in vacuum 10\textsuperscript{-6} mm Hg during 2 h at 673 K before all the kinetic experiments, it was a standard treatment. XRA (Rigaku Ultima IV, Japan) and XR fluorescence spectroscopy (express analyzer Niton, USA) were used to obtain the information about phase and elemental composition of the foil before and after adsorption/desorption experiments. No significant difference in faze structure showed XRA data for “fresh” and “worked” foil. Not only that \(Y_2O_3\) was found for both samples (in the lesser extent in second sample). The similar result gives XRFS data: the content of Y decreases in 27%. The hardness also decreases from 300 to 160 kg/mm\textsuperscript{2} at 100 kg/mm\textsuperscript{2} of loading (Vickers method, LECO-V-400H).

3. Results and discussions

3.1. Hydrogen sorption

We have carried out two series of experiments: in lower H\textsubscript{2} initial pressure (0,002±0,016 mm Hg) and in higher pressure (>0,016 mm Hg). The typical kinetic curves are shown in figure 1 only for tree \(P_0(\text{H}_2)\) in test 1 of series I. The shape of sorption curve might give us the information about order of sorption process. But we preferred to calculate the rate of sorption in the start for interval 0-1 minute. Initial \(W_s\) at \(t\to0\) characterizes the state of initial active adsorption/sorption sites. The first order is common, but in some earlier publications the fractional order \(2 > n >1\) was considered. We observed in this study the liner dependences of \(W_s\) from H\textsubscript{2} pressure (figure 2), so the rate constants of H\textsubscript{2} sorption were obtained without any connections with \(n\). The similar result for two series was the decrease of \(K_s\) in repeated experiment and in series I and II with the same ratio \(K_s(1)/K_s(2)=1.6\) and \(K_s(I)/K_s(II)=15.5/3.9=9.3/2.4=4\) (table 2). So the preadsorbed hydrogen in subsurface form inhibits the sorption.

![Figure 1. Kinetic curves of hydrogen sorption at 333 K and various initial H\textsubscript{2} pressure 0.016 (1), 0.008 (2), 0.004 (3) mm Hg.](image-url)
The temperature of sorption doesn’t influence the shape of kinetics curves of H₂ sorption. The rate constant $K_s$ obeys in Arrhenius-type rate low (figure 3) and the apparent activation energy increases in two times – $E_{a,1} = 3$ and $E_{a,2} = 6$ kJ/mol. This result is in good agreement with kinetics sorption data about the diminishing sorption activity after test 1 despite the vacuum treatment of foil at 673 K 0.5 h between experiment 1 and 2. Hydrogen would prefer to stay inside PdY rather than on the surface and not remove by heating standard procedure. So subsurface chemisorbed H deactivates the surface sites on which the dissociative adsorption occurs.

### Table 2. Hydrogen sorption: the constant rate values $K_s$ [molecules-min⁻¹-mm Hg] in two series (I and II) for in first (1) and second (2) tests.

| $P_0$ (H₂) in mmHg | 0.002 ± 0.016 (I) | 0.016 ± 0.04 (II) |
|-------------------|------------------|------------------|
| Experiment number | 1  | 2  | 1  | 2  |
| $K_s \cdot 10^{-13}$ | 14.7 | 9.4 | 3.9 | 2.4 |
| $K_s(1)/K_s(2)$ | 1.6 | 1.6 |  |

3.2. Hydrogen desorption

After foil exposure in pure H₂ at room temperature during 24 h (I) and 4 days (II) and evacuation of gaseous faze (0.5 h) the temperature rises step by step and in isothermal conditions the desorption curves were obtained. The time dependences of amount of H₂ desorbed, monitored during 5 min. were not linear, but in the quick period $t \rightarrow 0$ up to 2 min. it were straight lines. Rate of desorption augments with temperature, but $W_{ds} - T$ dependences and show a maximum (figure 4). The values of constant rates of desorption only increase with $T$. Supposing first or second order the rate constant of desorption process is defined $K_{ds,1} = W_{ds}/\theta$ or $K_{ds,2} = W_s/\theta^2$, where coverage $\theta = N_{ds}/N_{max,ds}$ depends on temperature and decreases sharply with temperature rise. Total (maximum) amount of desorbed H₂ molecules $N_{max,ds}$ was $227 \cdot 10^{15}$ (I) and $14 \cdot 10^{15}$ H₂ molecules (II), so we observed the similarity between sorption and desorption kinetic data. The effect of very small amount $N_{max,ds}$ after saturation foil by hydrogen (long time exposure) indicates the decreases the adsorption due to residual H presence in the Pd bulk. The linear dependence $\ln K_{ds} - T^{-1}$ in Arrhenius plots of desorption is better than 0.99 (figure 5). The values of activation energy of hydrogen desorption calculated from $K_{ds}$ for assumed first $n=1$ (H₂-s $\rightarrow$ H₂↑) and second $n=2$ (2H-s $\rightarrow$ H₂↑) order are shown in table 3.
Figure 4. The temperature dependences of the rate of H$_2$ desorption ($W_{\text{des}}$, molecules$\cdot$min$^{-1}$) from PdY foil in series I ($\circ$) and II ($\bullet$).

Figure 5. Arrhenius plot of the constant rate of H$_2$ desorption in II: H$_2$ pressure = 0.0092 mm Hg, n=1.2.

Table 3. Hydrogen desorption: the activation energy calculated from Arrhenius plots of constant rate of H$_2$ desorption in first (1) and second (2) tests.

| Kinetic order | n = 1 | n = 2 |
|---------------|-------|-------|
| Number test   | 1     | 2     | 1     | 2     |
| $E_a$ des, kJ/mol | 56    | 68    | 85    | 108   |
| $\ln K_0$ des | 51.4  | 50.0  | 58.9  | 59.6  |
| $r$           | 0.992 | 0.998 | 0.998 | 0.999 |

So, we observed in this study a similarity between the shape of desorption curve “desorption rate –temperature” and hydrogen desorption energy characteristics in repeated measurements: values of desorption activation energy $E_{\text{ades}}$ have a tendency to augment and in greater degree in case of second desorption order. Preadsorbed hydrogen inhibits the adsorption of higher bounded hydrogen.

3.3 Isotherms of hydrogen adsorption in dynamic mode

In this adsorption measurements the Pd–7%Y alloy was subjected to several hydrogen flows throw capillary into the cell with palladium foil at room temperature (298 K) in consecutive tests (the input H$_2$ pressure in entrance of capillary was constant 0.074 mm Hg). Two isotherms were obtained for initial state of foil after only treatment in vacuum 5 h at 673 K – lines 1 and 2 correspond for the fist and the second tests, between 1 and 2 it was only outgassing 15 min at 298K. The next experiments have been done after kinetic measurements of hydrogen adsorption and desorption with results, discussed above. Isotherm 3 was obtained without heating in vacuum at high temperature, but line 4 – after 1 h vacuum treatment at 673 K (between 4 and 5 outgassing, 15 min, 298K). The isotherms of hydrogen adsorption 1-5 are shown in fig.6. It can be seen the nonlinear isotherm shape for hydrogen adsorption (sorption). Such form of isotherm was analyzed earlier in our work for the model of the interaction between two dimensional electron gaze and ions and molecules adsorbed, that led to inducing adsorption on metal surface [10]. The preadsorbed or dissolved species change the state of surface unfilled sites and their influence can be taken into account by virial coefficients $B_{11}$ (is constant) and $B_{12}$ (depends on adsorbates charge). For neutral or very small negative and positive charge, for example H, H$^+$, H$_2$-3, H$_2$+6, H$^{3+}$ [11], $B_{12}$ < 0 and isotherm shape is the concave line. In case of $B_{12}$ > 0 the isotherm is a convex line in coordinates adsorbed quantity ($N_{\text{ads}}$) vs pressure.
The equation (1) represents a linearized form of isotherms with induced adsorption. Good linearization of the experimental results obtained (fig.7) shows a good description of such model for hydrogen-palladium system too.

$$\ln \left( \frac{N_{ads}}{P} \right) = A - DP = \left( \ln A - \frac{Q_m}{RT} \right) - \left( B_{B_0} \frac{B_1}{B_{B_1}} \frac{C}{RT} \right) \cdot P$$

(1)

The parameters A and D were defined from semilogarithmic dependences \( \ln(N_{ads}/P) - P \) (table 4).

In the absence of bulk hydrogen (untreated in hydrogen sample) the amount of \( N_{ads} \) greater (1,2) than for the same sample of PdY foil “worked” in adsorption-desorption tests. In fact, the saturation the PdY foil in hydrogen, that remains in a bulk of the metal, decreases the adsorption (compare 1 and 3) so the summary charge of adsorbent surface is changed, as well as a subsequent adsorption test without thoroughly vacuum outgassing (dotted line). The D parameter drops in \( 2.535/1.864=1.34 \) (II) and \( 0.942/0.651=1.45 \), when for A the deviation not more than 1% (1,2 and 4,5) or 2.5% (1,3). These results agree well with data of sorption/desorption kinetic data.

**Figure 6.** Adsorption isotherms of \( \text{H}_2 \) on PdY.

**Figure 7.** The isotherms 3, 4, 5 in coordinates of Eqs. (1).

**Table 4.** Parameters of isotherms for induced adsorption of hydrogen on Pd–7%Y.

| Test | I. Before kinetics experiments | II. After kinetics experiments |
|------|-------------------------------|-------------------------------|
|      | 1                             | 2                             | 3                             | 4                             | 5                             |
| A    | 43.5                          | 43.0                          | 42.4                          | 42.7                          | 42.8                          |
| D    | 2.535                         | 1.864                         | 0.599                         | 0.942                         | 0.651                         |
| r    | 0.960                         | 0.991                         | 0.989                         | 0.992                         | 0.994                         |

4. **Conclusions**

The palladium-yttrium alloy 93%Pd–7%wt.Y that represent a considerable importance for the technology of hydrogen diffusion alloys and membrane catalysts was studied with regard to its adsorption and desorption properties. The kinetic characteristics of hydrogen adsorption and desorption with different conditions of \( \text{H}_2 \) uptake by PdY foil were obtain and analyze. The opinion that preferential absorption of hydrogen by these subsurface sites would facilitate hydrogen diffusion into the bulk of the metal can be added by our data from isotherms, that may be explained by inducing adsorption model. The main result of this work is the experimental improve the inhibiting of adsorption capacity of the foil surface by preliminary dissolved hydrogen.
5. References

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