

Kinetics of changing in optical transmittance of palladium nanolayers during interaction with hydrogen

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The kinetics of changing in optical transmittance of palladium (Pd) nanolayers (about 10 nm thick, deposited on object glass substrates by thermal evaporation in vacuum) in hydrogen flow (100% H₂) in the temperature range of 300–335 K are studied. It is shown that the rate of changing of palladium optical transmittance at hydrogen flow rises linearly with increasing the temperature due to sorption of hydrogen by Pd layer. The rate of changing in optical transmittance of Pd layer during sorption and desorption of hydrogen is established to rise by about one order with increasing the temperature from 300 to 335 K. The curves describing the changing in optical transmittance of palladium nanolayer during hydrogen desorption have two distinct sections: linear and nonlinear. The linear section of the curve weakly depends on temperature, while the nonlinear section sharply rises with increasing the temperature. Such the changing of the rate in optical transmittance can be associated with phase transition from β - to α -phase during hydrogen desorption from palladium.

Keywords: palladium, hydrogen, hydrogen sensor, palladium hydride, phase transition.

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Introduction

Palladium is used in a variety of industries because of its exceptional ability to absorb hydrogen and high rate of hydrogen diffusion in it [1–3]. Hydrogen dissolved in palladium causes deformation of the crystal lattice of the metal, which leads to changes in its properties: mechanical [4,5], electrical [2,6] and optical [3,7,8]. Such unique changes in the properties of palladium in contact with hydrogen make the platinum group metal the most sought-after element in the creation of hydrogen storage batteries [9] and hydrogen sensors [10–13].

Under hydrogen interaction with palladium a transition from α to β -phase takes place, which can be reversible [7]. The phases of the palladium-hydrogen system qualitatively differ in their physical properties. Thus, the α -phase corresponds to a low concentration of hydrogen dissolved in palladium (at their atomic ratio up to 0.03), the lattice constant of palladium in this phase 3.891 Å. An increase in hydrogen concentration from 0.03 to 0.6 in palladium leads to the formation of a mixed phase $\alpha + \beta$, and the lattice constant of palladium in this phase changes from 3.895 to 4.026 Å. A further increase in hydrogen concentration (> 0.6) leads to the formation of the β -phase, which corresponds to palladium hydride PdH [14].

The present paper is devoted to the study of the effect of temperature on the kinetics of changing in the optical transmittance of palladium nano-films in interaction with hydrogen and is the continuation of our works [7,15].

Experiment

Palladium layers 10–14 nm thick for various samples were obtained by thermal vacuum deposition of palladium metal (palladium mass fraction 99.96%) on glass substrates 1.5 mm thick (object glass), 20 mm² area at 10⁻⁶ residual pressure in a VUP-4 setup in contained volume. Prior to deposition of the palladium layers, the surface of the glass substrates was cleaned in OP-10 surfactant solution, then treated in NH₄OH/H₂O₂/H₂O peroxide-ammonia solution and washed in deionized water.

The thicknesses of the obtained Pd layers were measured using a Dektak 3030 profilometer and a Rigaku SmartLab X-ray diffractometer (CuK α , 40 kV, 200 mA). To study the kinetics of changing in optical transmittance during interaction with hydrogen, a typical sample with a Pd-layer thickness of 11 nm was chosen.

To measure the Pd-layer transmittance, the test sample was placed in a specially made sealed cuvette of 350 cm³ volume with inlet and outlet valves, through which alternate purging with hydrogen (100%) and atmospheric air was performed (Fig. 1). The cuvette was equipped with electrical leads to supply power to the LED, an electrical contact to the sample under study, and a contact to the photodiode. The sample under study was fixed on the textolite board so that the Pd-layer adhered to the copper contacts of the board. The Pd-layer was heated by passing a direct electric current through the copper contacts of the textolite board to make measurements at an elevated temperature. The sample temperature was monitored using a temperature sensor

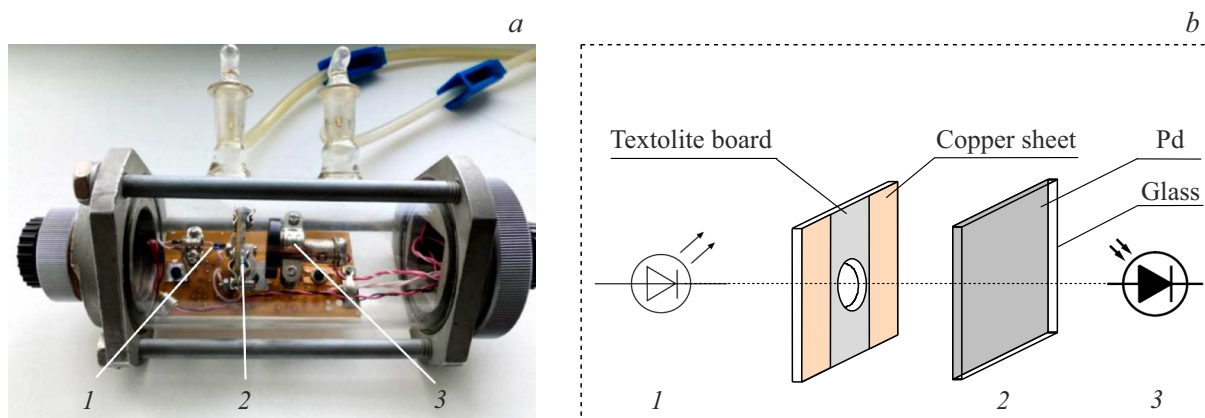


Figure 1. Picture (a) and block scheme (b) of the measuring cuvette: 1 — LED ($\lambda = 0.94 \mu\text{m}$), 2 — palladium film on object glass, 3 — photodetector.

(Honeywell HEL700-U-1-A). The optical transmittance of the Pd layer was determined by measuring the intensity of the light emitted by an LED (Vishay, TSAL4400) through the hole in the textolite board and sample. The intensity of the light passing through the sample was registered with a silicon photodetector. The optical transmittance of the Pd-layer, which is proportional to the photodetector current, was measured in the temperature range of 300–335 K.

To confirm the established in [15] phase transition in palladium nanofilm-hydrogen system, an experiment was conducted in which a Pd film sample was placed in a specialized chamber equipped with a hydrogen purge system. Hydrogen was obtained from the interaction of metallic zinc with hydrochloric acid. The hydrogen produced by the chemical reaction was purified in two stages by passing it through water gates. The sample was blown with hydrogen for 100 s, after which the chamber was sealed and mounted on a Rigaku SmartLab X-ray diffractometer ($\text{CuK}\alpha$, 9 kVt). Diffraction patterns were measured in the sliding incidence X-ray beam geometry (GiXRD).

Results and their discussion

The kinetics of changing in the optical transmittance T/T_0 of the Pd layer with a thickness of $d = 11 \text{ nm}$ was studied in the temperature range of the sample 300–335 K (Fig. 2).

At the beginning of the experiment in the time interval $t = 0\text{--}60 \text{ s}$ the sample is in the atmospheric air environment. When H_2 flow is passed through the measuring cuvette at 300 K at the time $t = 60 \text{ s}$, the palladium optical transmittance increases by $\sim 23\%$ for 8 s. Then the Pd-layer is saturated with hydrogen and the optical transmittance reaches its maximum value. After starting to purge the cuvette with atmospheric air (since the time $t = 200 \text{ s}$), the optical transmittance of palladium decreases to its initial value for 140 s. Thus, the rate of increase in the optical transmittance of the Pd-layer with hydrogen blowing is

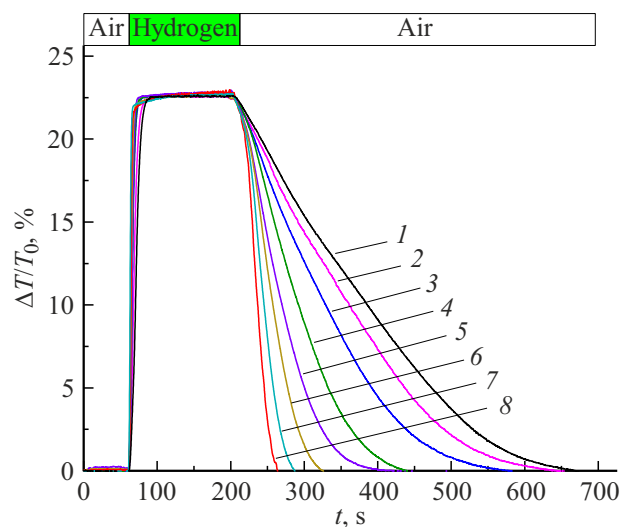


Figure 2. Optical transmittance changing of the Pd-layer when exposed to H_2 at different sample temperatures. Temperature, K: 1 — 300, 2 — 305, 3 — 310, 4 — 315, 5 — 320, 6 — 325, 7 — 330, 8 — 335.

almost an order of magnitude higher than the rate of reduction of the optical transmittance of the Pd layer with atmospheric air blowing.

As it follows from Fig. 2, the changing in the optical transmittance of the Pd-layer consists of three stages: first stage — the rapid linear growth of the optical transmittance as a result of hydrogen adsorption followed by dissolution in the Pd-layer; second stage — the output of the dependence curve $\Delta T/T_0$ from t to a constant level, which is associated with saturation of the Pd-layer with hydrogen; third stage — smooth decrease in the optical transmittance of the Pd-layer due to the process of hydrogen desorption when the sample is blown with atmospheric air. Hydrogen desorption is slower than the sorption process, so the rate of decrease in transmittance is less than the rate of growth of this parameter during the stage of sorption. It should

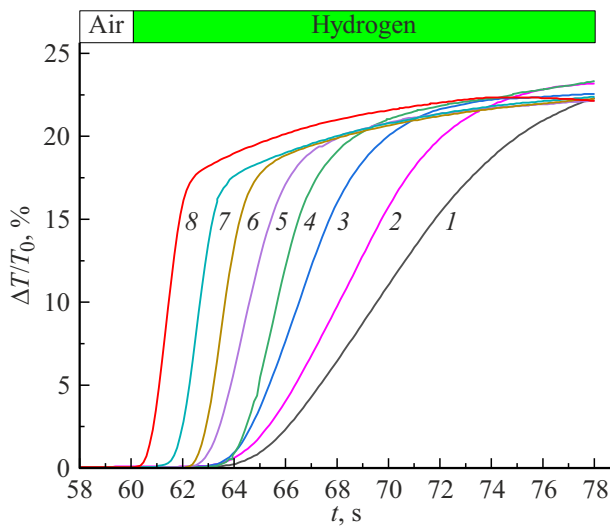


Figure 3. Kinetics of changing in optical transmittance of the Pd-layer as a function of temperature. Temperature, K: 1 — 300, 2 — 305, 3 — 310, 4 — 315, 5 — 320, 6 — 325, 7 — 330, 8 — 335.

be noted that hydrogen sorption and desorption accelerate with increasing sample temperature. This should result in a faster change in optical transmittance. For example, with hydrogen flow through the cuvette at 335 K, the Pd optical transmittance increases to its maximum in about 1 s, which is almost 10 times faster than at room temperature (Fig.3). The hydrogen desorption process at 335 K takes about 40 s compared to ~500 s at 300 K (Fig. 2).

Let us consider in more detail the stages of hydrogen sorption and desorption and their influence on the optical transmittance of the Pd-film. Fig. 3 shows that when the sample temperature increases, the process of hydrogen sorption and optical transmittance growth starts at an earlier time. The kinetics of changing in optical transmittance at this stage can be approximately described by a linear function whose slope tangent is equal to the growth rate of a given value ($S = d(\Delta T/T_0)/dt$).

Fig. 4 shows the dependence of the rate of changing in optical transmittance S on the temperature of the Pd layer. As can be seen, this dependence has a linear character, thus, an increase in temperature leads to a uniform acceleration of the hydrogen sorption process.

Let's move on to the examination of the change in the optical transmittance of the Pd layer after H_2 supply termination and blowing samples with atmospheric air on an enlarged scale (Fig. 5). As the temperature increased, the rate of hydrogen desorption in the samples studied increased. If we look carefully at Fig. 5, we can see that when the temperature rises, two characteristic areas appear after the start of atmospheric air purging the cuvette: linear I and non-linear II. At room temperature, the optical transmittance curve has a long linear section and a short nonlinear section. In the linear section I, the rate of palladium transmittance recovery and, correspondingly, the

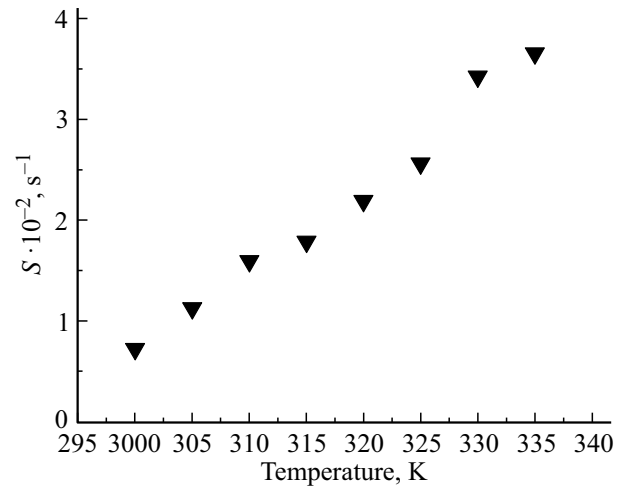


Figure 4. The rate of changing in optical transmittance of the Pd-layer at different sample temperatures.

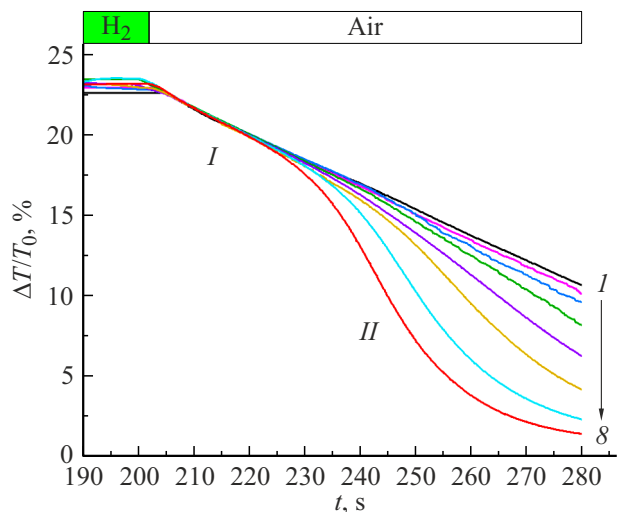


Figure 5. Kinetics of changing in optical transmittance in hydrogen desorption at different temperatures. Temperature, K: 1 — 300, 2 — 305, 3 — 310, 4 — 315, 5 — 320, 6 — 325, 7 — 330, 8 — 335.

rate of hydrogen desorption weakly depend on temperature. At section II, the kinetics of change in optical transmittance is nonlinear and is well described by a function of the form

$$T = A \exp\left(-\frac{t}{\tau}\right),$$

where T — transparency of the Pd-layer, A — coefficient proportional to temperature, t — time, τ — time constant of Pd-layer optical transmittance recovery. With increase the temperature from 300 to 335 K the time constant of transmittance recovery decreases linearly from 124 to 15 s. The observed changing in transmittance kinetics in Fig.5 may be due to $\beta \rightarrow \alpha$ phase transition in the process of hydrogen desorption from palladium, where areas I and II characterize β and α -phases, respectively.

Fig. 6 shows a graph of the rate of changing in optical transmittance vs. time during hydrogen desorption process. On the graph, we can see a narrowing of the area corresponding to the mixed ($\alpha + \beta$)-phase with increasing temperature. This effect is consistent with the phase diagram for the palladium–hydrogen [1,3,5,16] system, namely with the reduction of the mixed phase existence interval as the temperature increases. Also worth noting is the jump change in the optical transmittance of the Pd-layer. A similar change in characteristics has been observed previously [15] and probably corresponds to a change in the $\beta \rightarrow \alpha$ phase in the palladium–hydrogen system at hydrogen concentrations of 10 and 1 percent, respectively. The acceleration of the sorption and desorption processes when the sample temperature is increased can be attributed to a decrease in the solubility [3,17] limit and an increase in the rate of hydrogen diffusion into the palladium [18].

Fig. 7 shows diffraction patterns of a Pd layer in 1) air before hydrogen sorption, 2) hydrogen atmosphere and 3) air after hydrogen desorption. A diffraction pattern of the sample before it was purged with hydrogen (Fig. 7, curve 1) shows Bragg peaks corresponding to α -phase palladium (ICSD 01-087-0643). After blowing the sample with hydrogen the Bragg peaks became consistent with β -phase PdH (ICSD 03-065-0557). Subsequent purging of the sample with air for 600 s resulted in a shift of the peaks back to the α -phase of metallic Pd.

Thus, the results of X-ray diffraction analysis confirm the formation of β -phase PdH as a result of hydrogen sorption by palladium, followed by transition to α -phase after desorption.

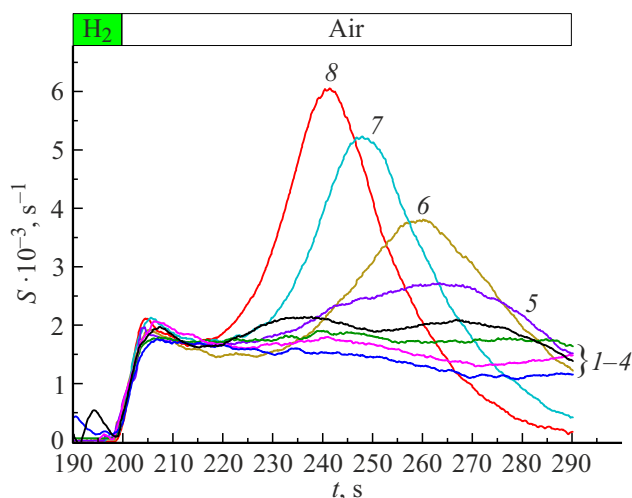


Figure 6. The rate of changing in the optical transmittance of the Pd-layer at different moments of time at different temperatures. Temperature, K: 1 — 300, 2 — 305, 3 — 310, 4 — 315, 5 — 320, 6 — 325, 7 — 330, 8 — 335.

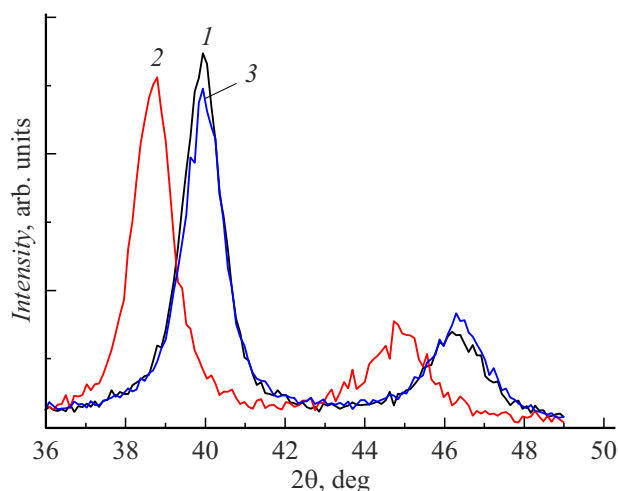


Figure 7. Diffraction patterns of Pd film: 1— α is the Pd phase in air medium, 2— β is the PdH phase in hydrogen atmosphere, 3— α is the Pd phase when returning the film to air medium.

Conclusion

The effect of temperature on the kinetics of changing in optical transmittance of Pd layer on glass substrate at alternating hydrogen and air flows in the temperature range 300 – 335 K was investigated. It is shown that the rate of increase in optical transmittance after contact of Pd nanofilm with hydrogen increases linearly with increasing temperature. When the hydrogen flow is replaced by atmospheric air flow, the optical transmittance of the palladium is recovered. In this case, the kinetic dependence curve shows two areas: linear and non-linear. The rate of transmittance recovery in the linear region, which corresponds to the palladium hydride state in the β -phase, is weakly dependent on temperature. The recovery rate in the nonlinear section increases with increasing temperature and is characterized by the α -phase. The change from linear to non-linear characteristic is most clearly seen at temperatures above 315 K and appears to characterize the phase transition from β - to α -phase.

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Conflict of interest

The authors declare that they have no conflict of interest.

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