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STUDY OF THE INTERACTION PROCESS OF PALLADIUM ALLOY WITH HYDROGEN IN α-REGION OF THE Pd-H DIAGRAM

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The influence of the rate of hydrogen supply into the chamber on the process of form − changing of a cantilever made of pure palladium and α-PdH_n alloy at a temperature of 150 °C was studied. It was shown that the process of hydrogen saturation of palladium occurs in two stages: rapid bending, reaching the maximum bending with the formation of a plateau, and gradual straightening of the cantilever to a stationary state. It was established that the rate of hydrogen supply into the chamber affects the kinetics of the process of deformation of the cantilever, the speed of reaching a stationary state.

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INTRODUCTION

With the rapid development of nuclear and hydrogen energy, as well as the creation of highly selective sensors, sensor devices, and cantilevers for atomic force microscopes, the interaction of hydrogen and its isotopes with metals is becoming increasingly important [1, 2]. One of the key objects for such studies is the Pd-H system [3–5]. The penetration of hydrogen into metals leads to the expansion of the metal crystal lattice and the emergence and redistribution of internal stresses [6–8]. These stresses lead to a number of hydrogen-elastic and hydrogen-plastic effects, including changes in the shape of the metal [9]. Hydrogen-saturated palladium has improved plastic properties compared to pure palladium: it is easier to undergo reverse elastic deformation [10, 11]; it has different mechanical properties [12, 13] than palladium without hydrogen, which is less flexible and more brittle.

Quite often, bilayer samples are studied, where a palladium nanolayer is applied to a silicon cantilever sample and the bending of these cantilevers and the processes of hydrogen penetration into the palladium film are investigated [14–16]. In this kind of experiments, hydrogen diffusion in palladium is not considered because of the transience of this process compared to the process of hydrogen penetration into palladium, given the small thickness of the palladium film (nanolayer) [14–16]. In addition, such experiments do not have good reproducibility due to the dependence of the cantilever deviation on the structure of the palladium film both on its free surface and on the surface of contact with the substrate.

In this paper, we propose and carry out an experiment to measure the bending-extension of a relatively thick cantilever made of pure palladium in a hydrogen-filled chamber; we perform an asymptotic analysis and present the time dependence of the deflection of the palladium cantilever.

METHODS AND APPARATUS

An advanced hydrogen-vacuum unit (HVU) was used for the experiments [10, 17]. The samples, made in the form of cantilevers (a plate with dimensions of 68×5.5×0.27 mm made of palladium with a purity of 99.9%), were coated with a 750 nm thick layer of copper, which is impervious to hydrogen, on one side using an electrolytic method [18, 19]. After that, the samples were heated in the HWU chamber to the experimental temperature (273+150 K) and kept for 30 min to reduce thermal stresses. Then, hydrogen saturation of pure palladium cantilevers was carried out to the state of α-PdH_n alloys, where n is a certain concentration of hydrogen in the alloy at a constant hydrogen pressure in the installation chamber. The resulting alloy was kept under isothermal conditions to relieve concentration stresses, after which additional one-sided saturation of the cantilever to the α-PdHn alloy was carried out, where n varies for each alloy by the same value. The process of changing the shape of the cantilever was recorded using a catheter and recorded on a video camera. The results were then interpreted and time dependencies of the cantilever shape change during the saturation process were plotted.

EXPERIMENT

A series of experiments was performed for the α-PdH_n cantilever, where $n_{i+1} = n_i + \Delta n$ varies for each alloy depending on the hydrogen pressure in the chamber (Table 1). A series of experiments was conducted where the concentration was changed by $\Delta n = n$, $\Delta n = 1.3n$, and $\Delta n = 1.1n$, respectively.

Table 1 shows the data on the change in the bending parameters of the palladium plate during the experiments with hydrogen penetration at different pressures, where P, MPa, is the hydrogen pressure during the injection; Δts, s, is the time of hydrogen injection into the chamber of the installation; Δtmax, s – time to reach the maximum bending of the cantilever; Y_{max}, mm – maximum bending of the cantilever; tp, s – duration of the plateau; Δtst, s – time to reach the stationary state (residual bending) of the cantilever; Yst, mm, is the value of the residual bending of the cantilever after relaxation; Δtad, s, is the duration of additional exposure of the cantilever in the hydrogen environment when the steady state does not change; n, H/Pd, is the ratio of the number of hydrogen atoms to palladium atoms (hydrogen concentration); Δn, H/Pd, is the addition of hydrogen concentration for the alloy; v, MPa/s, is the rate of hydrogen injection to a given pressure into the installation chamber. The time dependences of the change in the shape of palladium cantilever were plotted (Fig. 1).

Table 1

Characteristics of cantilever shape changing at the rate of hydrogen supply to the chamber 0.01 MPa/s

№	P, MPa	Δt_s, s	Δt_{max}, s	Y_{max}, mm	tp, s	Δt_{st}, S	Y_{st}, mm	Δt_{ad}, s	n, H/Pd	Δn, H/Pd	v, MPa/s
1	0.01	1.0	16	1.38	10	600	0.21	1800	0.00767	0.0077	0.01
2	0.037	2.6	28	1.89	33	690	0.34	810	0.01770	0.0100	0.01
3	0.061	2.5	36	1.77	33	1200	0.51	3600	0.02646	0.0088	0.01

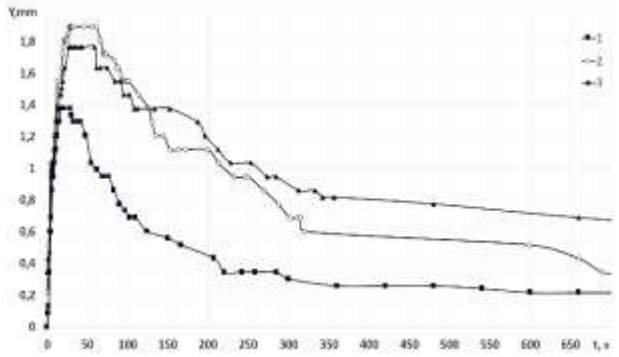

Fig. 1. Time dependences of cantilever shape change 1 − for pure palladium; 2 − for α-$PdH_{0.0077}$ alloy; 3 − for α-$PdH_{0.0177}$ alloy at a hydrogen injection rate of 0.01 MPa/s

Fig. 1 shows that the saturation process of cantilever from pure palladium and α-PdH_n alloy is carried out in two stages. For pure palladium (curve 1) and α-$PdH_{0.0077}$ and α-$PdH_{0.0177}$ alloys (see Fig. 1, curves 2, 3), at the first stage, the cantilever bends rapidly immediately after the hydrogen is introduced into the chamber of the hydrogen-vacuum unit. At the same time, when the pressure gauge reaches the appropriate pressure (P) over time (Δt_s, s), which ensures the production of an alloy with the required concentration (n, H/Pd), the bending of the cantilever in all cases reaches an experimentally detectable value and continues to increase until it reaches the maximum value (Y_{max}, mm), and then a plateau with a duration of (tp, s) of several seconds is observed, and then the second longer stage of cantilever straightening begins with the achievement of a stationary state (Y_{st}, mm) over a certain time (Δt_{st}, s), which does not change during additional exposure (Δt_{ad}, s).

Let us consider in more detail one of the experiments (see Fig. 1, curve 2), when the cantilever from the α-$PdH_{0.0077}$ alloy is saturated, when the concentration changes to Δn = 0.001 H/Pd and hydrogen is injected to a given pressure of 0.036 from 0.01 MPa into the chamber for 2.6 s at a rate of 0.01 MPa/s, the cantilever bending continues to increase and reaches its maximum value of Y_{max} = 1.89 mm in 28 s from the moment of the start of hydrogen injection into the chamber (see Fig. 1, curve 2). Next, we observe the formation of a plateau from the 28th second, which lasts 33 s (see Fig. 1) and the cantilever is in a bent maximum position, after which it begins to straighten and the bending arrow decreases. This second stage is almost 20 times longer than the first stage, see Fig. 1, curve 2. After 690 s from the beginning of the experiment, the cantilever reaches a stationary state (Y_{st} = 0.34 mm), which does not change during the subsequent long exposure of 810 s.

Interestingly, if we increase the pressure in the chamber from 0.036 to 0.061 MPa at Δτs = 2.5 s, and create an α-$PdH_{0.0264}$ alloy when the concentration changes by Δn = 0.0087, which is a smaller value than in the previous experiment, we experimentally recorded a smaller maximum bending of the cantilever (Y_{max} = 1.77 mm) at $\Delta\tau_{max}$ = 36 s (see curve 3 in Fig. 1) from the beginning of hydrogen injection into the chamber. Next, we observe a plateau lasting 33 s, after which the cantilever begins to straighten gradually, and this process slowed down over time until reaching a certain stationary state (Y_{st} = 0.51 mm) after 1200 s. Additional exposure for 3600 s did not lead to a change in the position of the cantilever.

The relaxation processes that started in the cantilever when it began to straighten indicate a gradual decrease in hydrogen concentration stresses and redistribution of hydrogen in the middle of the palladium crystal lattice from the surface to the middle of the cantilever.

Analysing curves 1, 2, 3 in Fig. 1, we can note that all curves have a similar shape, which indicates a similar mechanism of hydrogen penetration, namely the effect of the hydrogen supply rate to the chamber and, accordingly, the effect on diffusion processes inside the palladium, but with different intensity. It should be noted that, although the concentration changed by almost the same amount, the value of the maximum bend for the α-$PdH_{0.0077}$ alloy (see curve 1, Fig. 1) is greater than for the α-$PdH_{0.0177}$ alloy (see curve 3, Fig. 1), and the time to reach the maximum bend at a constant hydrogen supply rate increases and is 16, 28, and 36 s, respectively. This indicates a slowdown in the rate of diffusion into the middle of the cantilever and redistribution of hydrogen in the middle of the sample, since some of the octahedral pores are already occupied and hydrogen has to migrate through the sample thickness to the middle through the tetrahedral pores, which requires some state. In addition, under bending conditions, hydrogen concentration stresses also create certain difficulties with diffusion into the sample. Accordingly, after the cantilever has been saturated with hydrogen at a certain concentration and the bending has reached its maximum value, we observe plateaus in Fig. 1, lasting 10, 33, 33 s, respectively, for each experiment. These plateaus indicate the establishment of a quasi-thermal-baroelastic-diffusion (TBED) equilibrium and the beginning of the sample relaxation process, which we observe at stage 2 (see Fig. 1, curves 1–3). It has been experimentally documented that the shape of the curves and the kinetics of the straightening process depend on the saturation rate of palladium and α-$PdH_{0.0077}$; α-$PdH_{0.0177}$ alloys. Thus, in the interval from 100 to 300 s, we can see a slowdown in the straightening process and the formation of temporary

plateaus, in the same time interval for curves 2 and 3 (see Fig. 1). It should be noted that the feed rate affects the course of the kinetic curves, the slope of the curve decline, and the speed of reaching the steady state. It has been experimentally established that when the α-PdH_n alloy is saturated with increasing hydrogen content, the residual bending of the cantilever after additional holding increases and amounts to 16, 18, and 28% (see Fig. 1, curves 1–3) relative to the maximum bending.

The results obtained need to be clarified and analysed in two more ways, when the hydrogen concentration in palladium changes by the same amount for different alloys and the rate of hydrogen injection into the HFO chamber changes. This will make it possible to compare the efficiency of hydrogen absorption under different conditions and may indicate some features of the kinetic processes of hydrogen interaction with the material.

To confirm this fact, we performed several more experiments by changing the hydrogen supply rate to the chamber for the alloys listed in Table 1. Thus, we additionally conducted experiments according to the method described above, when we reduced the hydrogen supply rate by almost 50 times to 0.0002 MPa/s, the results of the experiment are shown in Table 2 and Fig. 2.

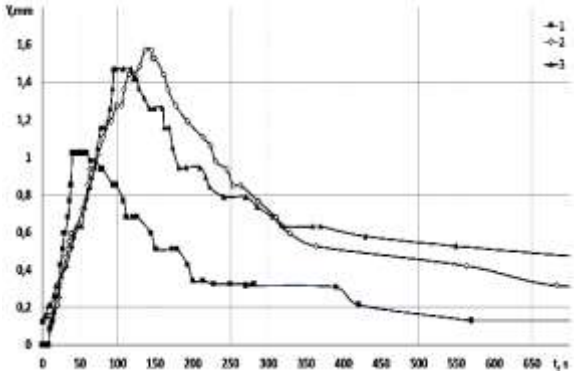

Fig. 2. Time dependence of cantilever deformation: 1 – for pure palladium; 2 – for α-$PdH_{0.0077}$ alloy; 3 – for α-$PdH_{0.0177}$ alloy at a hydrogen injection rate of $2\cdot10^{-4}$ MPa/s

Fig. 2 shows that when the rate of hydrogen injection into the chamber changes by a factor of 50 from 0.00022 to 0.00026 MPa/s, the increase in maximum bending occurs in proportion to the time of hydrogen injection into the chamber. After the hydrogen supply to the chamber is stopped, the maximum bending also stops increasing (curves 1–3). Then, for each experiment, we record the presence of a plateau of different duration: 19, 12, and 24 s. It should be noted that curves 1 and 3 correspond to saturation with velocities of 0.00025 and 0.00026 MPa/s, respectively, and Fig. 2 shows that the kinetics of the plate return to the stationary state is identical: we observe the establishment of the second plateau from 94 to 98 s for curve 1, which is mirrored in curve 3 from 142 to 159 s. The straightening process then proceeds smoothly again, but then we observe 3 plateaus in the interval from 112 to 126 s for curve 1, and a similar plateau is observed in curve 3 from 181 to 209 s. Then, again, the straightening process proceeds slowly with the formation of another plateau in curve 1 in the interval 151…179 s and for curve 3 at 241…270 s. If we further examine the kinetics of cantilever straightening, we can notice the presence of other plateaus in curves 1 and 3, the duration of which increases, and the sample gradually returns to its original position with some residual bending, which does not change during prolonged exposure to hydrogen and is 0.13 mm for the newly created α-$PdH_{0.0077}$ fame and 0.42 mm for the α-$PdH_{0.0265}$ alloy.

For the second experiment (see curve 2 in Fig. 2), the build-up was carried out at a different, slightly lower rate of 0.00022 MPa/s and, as can be seen, the process of forming the maximum bend also stops after the end of the hydrogen supply to the chamber. However, the duration of the plateau is shorter than for curves 1 and 3 and is 12 s. Further, we observe a gradual decrease in the maximum bend, but the kinetics of the process differs from curves 1 and 3: there are no more plateaus and the straightening process is quite smooth.

To confirm the fact that the hydrogen supply rate to the HWU chamber affects the nature of the cantilever straightening curve after reaching the maximum bend, we conducted an experiment when the supply rate was reduced by almost 200 times compared to experiment 1 (see Table 1). The temperature and pressure of the experiment were left unchanged; the results of the experiment are shown in Table 3 and Fig. 3.

Table 2

Characteristics of cantilever shape changing at the rate of hydrogen supply to the chamber $2\cdot10^{-4}$ MPa/s

№	P, MPa	Δt_s, s	Δt_{max}, s	Y_{max}, mm	tp, s	Δt_{st}, S	Y_{st}, mm	Δt_{ad}, s	n, H/Pd	Δn, H/Pd	$v\cdot10^{-4}$, MPa/s
1	0.010	40	40	1.10	19	570	0.13	3600	0.00767	0.0077	2.50
2	0.037	120	120	1.57	46	1600	0.10	3600	0.01778	0.0101	2.25
3	0.061	90	90	1.47	63	900	0.42	3600	0.02646	0.0088	2.67

Table 3

Characteristics of cantilever shape changing at the rate of hydrogen supply to the chamber $5\cdot10^{-5}$ MPa/s

№	P, MPa	Δt_s, s	Δt_{max}, s	Y_{max}, mm	tp, s	Δt_{st}, s	Y_{st}, mm	Δt_{ad}, s	n, H/Pd	Δn, H/Pd	$v\cdot10^{-4}$, MPa/s
1	0.010	207	78	0.69	27	600	0.10	600	0.00767	0.0077	2.5
2	0.037	505	484	0.93	59	1133	0.19	1133	0.01778	0.0101	2.25
3	0.061	490	186	0.77	138	1588	0.26	1588	0.02646	0.0088	2.67

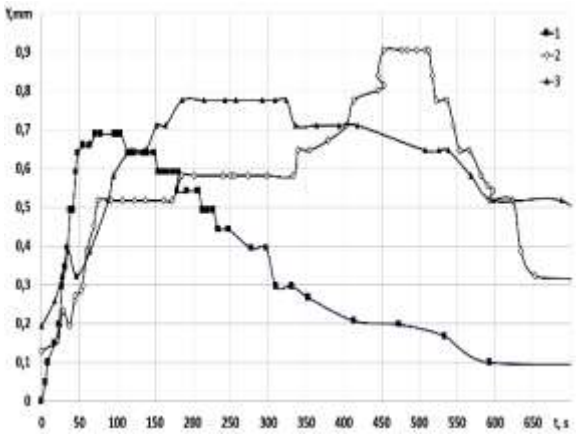

Fig. 3. Time dependences of cantilever shape change: 1 – for pure palladium; 2 – for α-$PdH_{0.0077}$ alloy; 3 – for α-$PdH_{0.0177}$ alloy at a hydrogen injection rate of $4.8 \cdot 10^{-5}$ MPa/s

Fig. 3 shows that at the first stage of cantilever deformation, the increase in maximum bending occurs in proportion to the time of hydrogen supply to the chamber, but the maximum bending is achieved already in the process of hydrogen supply to the chamber at 78, 484, and 186 s (see Fig. 3, curves 1–3, respectively) and is accompanied by the formation of a long-term plateau for 27, 59, 138 s, which increases with increasing hydrogen content in the α-PdH_n alloy. At the second stage of the formation process, the cantilever gradually begins to straighten with the formation of numerous short-lived plateaus, although the process of hydrogen supply is still ongoing. It should be noted that for curves 1 and 3, the hydrogen supply to the chamber was almost the same, approximately $4.9 \cdot 10^{-5}$ MPa/s, and the straightening kinetics is very similar, unlike curve 2, where the injection rate was less than $5.3 \cdot 10^{-5}$ MPa/s. Thus, at the first stage of deformation, the time of reaching the maximum bend is accompanied by the formation of long plateaus in the process of hydrogen injection and a gradual increase in the maximum bend to 0.93 mm at 484 s and the formation of a plateau lasting 59 s (see Fig. 3, curve 2), which continues to last even after the hydrogen supply to the chamber is stopped (505 s). The second stage of deformation here is characterised by a smooth and slow straightening with plateau formation, but in a smaller amount than we see in comparison with curves 1 and 3, and the return of the plate to a stationary state with a residual bending value of 21% of the maximum. For curve 1 (see Fig. 3), after 600 s from the start of hydrogen injection into the chamber, the residual bending is 14% of the maximum bending and remains unchanged during 480 s of short-term exposure. For curve 3, after 1600 s, the residual bending is 33% of the maximum bending and remains unchanged during 780 s of additional holding time.

Therefore, it can be concluded that the hydrogen supply rate during saturation of pure palladium (see Fig. 3, curve 1) and its α-PdH_n alloy (see Fig. 3, curves 2 and 3) affects the magnitude, time to reach the maximum bend, the kinetics of reaching this bend, the time of plateau formation at the moment of reaching the maximum bend, the kinetics of straightening and returning the cantilever to its original state. To exclude the influence of the addition of different amounts of hydrogen during each batch, we additionally conducted experiments according to the described methodology, when we changed the hydrogen content in palladium by one value Δn, the results of the experiment are shown in Table 4 and Fig. 4.

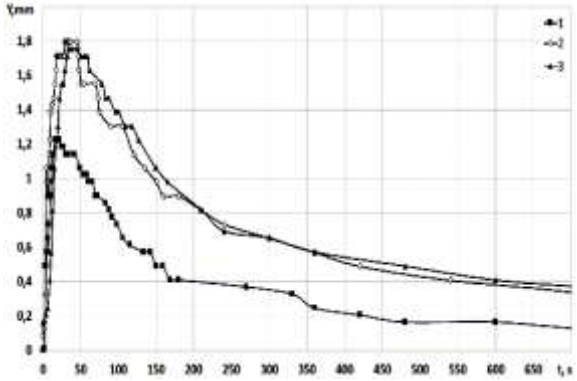

Fig. 4. Time dependences of cantilever shape change: 1 – for pure palladium; 2 – for α-$PdH_{0.0084}$ alloy; 3 – for α-$PdH_{0.0169}$ alloy when the concentration changes by 0.0084H/Pd and the hydrogen injection rate into the chamber is 0.01…0.007 MPa/s

As can be seen (see Fig. 4), a change in the hydrogen concentration by the same value did not cause significant changes in the kinetics of the cantilever shape change at both stages of its hydrogen saturation. When the concentration changes by Δn = 0.0084 H/Pd for cantilevers 1– from pure palladium; 2– α-$PdH_{0.0084}$ alloy; 3– α-$PdH_{0.0168}$ alloy from the beginning of hydrogen injection in the interval from 16 to 34 s, the curves show a rapid increase in the cantilever bending to a maximum value of about 1.26 mm (for curve 1), 1.79 mm (curve 2) and 1.75 mm (curve 3). Then, for each curve, a plateau is observed with a duration of: 6, 16, 11s, followed by a gradual decrease in bending, which is evident in the decline of the curves. As can be seen, curves 2 and 3, after 60 s from the beginning of the tension, have the same shape and angle of inclination, and after 200 s the decline continues and the bend reaches approximately 2 times less, namely 0.8 mm, and the straightening process proceeds identically for some time. Starting from 400 s for the second curve, we observe a more rapid decrease in the bending value, and by 900 s both curves reach a stationary state with a residual deformation value of 0.16 and 0.32 mm, respectively. It should be noted that with increasing hydrogen content in the alloy, the residual deformation increases and amounts to 6, 9 and 18% (see respectively for curves 1–3, Fig. 4) relative to the maximum bending. In Fig. 4, curves 2 and 3 correspond to the experiment with a hydrogen supply rate of 0.0065 MPa/s to the test chamber and demonstrate that the straightening process proceeds identically. This confirms the hypothesis that the feed rate affects the speed and nature of the plate straightening and return to the stationary state.

It should also be noted that the same additions of hydrogen concentration (Δn = 0.00844 H/Pd) at saturation of α-$PdH_{0.0084}$ and α-$PdH_{0.0168}$ alloys, as well as the rate of hydrogen supply to the chamber at

saturation of the cantilever, affect the kinetics of achieving maximum bending and straightening of the plate. The identity of the straightening process is also characterised by curve 1 (see Fig. 4).

This indicates that the process of reducing hydrogen concentration stresses obeys the same dependencies when the concentration changes by the same amount and at the same rate. The most interesting thing is that the saturation rate and the process of forming the maximum bend affect the kinetics of straightening and returning the plate to a stationary state. It is interesting to analyse another fact if the additive Δn = 0.009 H/Pd for the 3 alloys is the same and the hydrogen supply rate is changed by a small amount (Table 5, Fig. 5).

Table 4

Characteristics of cantilever shape change when the hydrogen content changes by Δ n = 0.0084 H/Pd

№	P, MPa	Δt_s, s	Δt_{max}, s	Y_{max}, mm	tp, s	Δt_{st}, S	Y_{st}, mm	Δt_{ad}, s	n, H/Pd	Δn, H/Pd	$v \cdot 10^{-2}$, MPa/s
1	0.011	1.0	16	1.26	6	1170	0.08	1200	0.0084	0.0084	1.12
2	0.034	3.5	17	1.79	16	900	0.16	3600	0.0169	0.0084	0.65
3	0.06	4.0	34	1.75	11	900	0.32	1200	0.0253	0.0084	0.67

Table 5

Characteristics of cantilever shape change when the hydrogen content changes by Δ n = 0.009 H/Pd

№	P, MPa	Δt_s, s	Δt_{max}, s	Y_{max}, mm	tp, s	Δt_{st}, S	Y_{st}, mm	Δt_{ad}, s	n, H/Pd	Δn, H/Pd	$v \cdot 10^{-3}$, MPa/s
1	0.036	5	37	3.41	6	780	0.21	1740	0.018	0.009	5.0
2	0.063	7	21	3.12	8	505	0.43	1475	0.027	0.009	3.9
3	0.088	6	27	2.97	14	660	0.5	2000	0.037	0.009	4.3

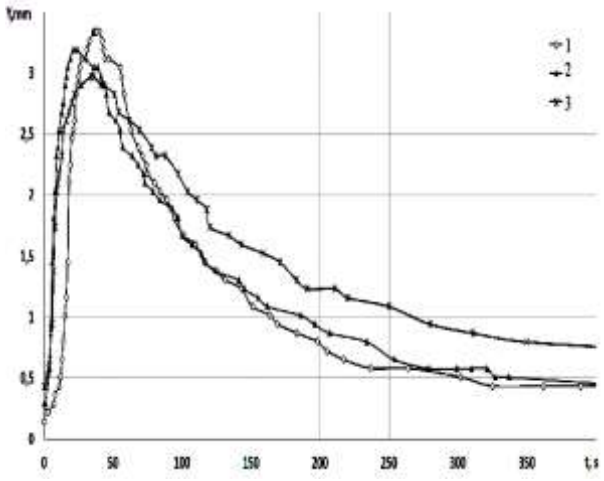

Fig. 5. Temporal dependences of cantilever shape change: 1 – for α-$PdH_{0.0084}$ alloy; 2 – for α-$PdH_{0.018}$ alloy; 3 – for α-$PdH_{0.027}$ alloy at a concentration change of 0.009 H/Pd

As can be seen (see Fig. 5), a change in the hydrogen concentration by the same value did not cause significant changes in the kinetics of the cantilever shape change at both stages of its hydrogen saturation. When the concentration was changed by Δn=0. 009 H/Pd for cantilever 1−for the α-$PdH_{0.0084}$ alloy, 2−for the α-$PdH_{0.018}$ alloy, 3− for the α-$PdH_{0.027}$ alloy from the beginning of hydrogen injection in the interval from 5 to 7 s, the curves show a rapid increase in the cantilever bending to a maximum value of about 3.41 mm (for curve 1), 3.12 mm (curve 2), and 2.97 mm (curve 3). Further, for curves 1, 2, 3 (see Fig. 5), a plateau (6, 8, 14 s) is observed, the duration of which increases and is followed by a gradual decrease in the cantilever bending. As can be seen, curves 1 and 2, corresponding to the experiment with the hydrogen supply rate to the chamber of the installation of 0.005 and 0.004 MPa/s, have the same shape and angle of inclination after 75 s from the start of the tension, and the straightening process proceeds identically for some time up to 140 s. Starting from 150 s for curve 2, we observe a smaller decrease in the bending value, and by 780 s the first curve reaches a steady state with a residual deformation value of 0.21 mm, and the second curve reaches a steady state of 0.43 mm after 500 s. For curve 3 (see Fig. 5), straightening proceeds similarly to curves 1 and 2 (see Fig. 5), but straightening and return to the initial state is slower and the residual deformation value of 0.53 mm is reached after 660 s from the start of hydrogen injection.

It should be noted that with an increase in the hydrogen content in the α-$PdH_{0.0084}$, α-$PdH_{0.018}$, α-$PdH_{0.027}$ alloys by Δn= 0.009 H/Pd, the residual deformation increases and is 6, 14, and 17% (see respectively for curves 1–3, Fig. 5) relative to the maximum bending.

The experiment confirms that with an increase in the hydrogen content in the alloy, when the concentration changes by the same amount (Δn=0.009 H/Pd): the time to reach the maximum bend is affected by the hydrogen supply rate; the duration of the plateau increases; the residual deformation increases, and the longer the hydrogen supply time, the longer it takes for the sample to return to the stationary state.

RESULTS AND DISCUSSION

An important role in the phenomenon under study is played by physical factors related to the peculiarities of the process of hydrogen penetration into palladium under our conditions, when the metal is subjected to internal concentration stresses and simultaneously undergoes a relaxation process. Let us consider the behaviour of cantilever:

Maximum bending (peaks): each graph has a pronounced maximum bending after the initial period of hydrogen saturation. This maximum bending corresponds to the moment when the hydrogen

concentration in palladium reaches a value that causes maximum deformation due to the expansion of the crystal lattice. Although the concentration changes by the same amount with each pass, the maxima appear at different times (Fig. 6), which is influenced by the rate of hydrogen supply to the chamber.

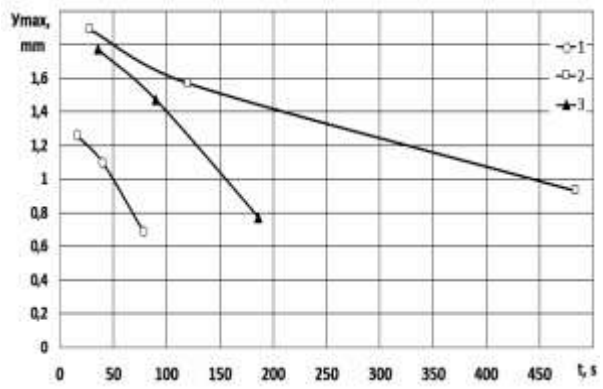

Fig. 6. Dependence of the maximum bending value on the time of reaching the maximum bending for 1, 2, 3 passes according to the results of the experiments in Figs. 1–3

Dependence of the maximum bending value (Y_{max}) on the time (t) of reaching the maximum bending for 1, 2, 3 passes (see Fig. 6) according to the results of the experiments presented in Table 1-3 when changing the concentrations in each pass by the same amount can be described by the following equations:

for pure palladium at 1 pass:

Y_{max} = -7E-05t^2 – 0.0029t + 1.3241;

for the α-$PdH_{0.0077}$ alloy at the 2nd pass:

Y_{max} = -1E-05 t^2 – 0.0041 t + 1.9325 ;

for the α-$PdH_{0.0177}$ alloy at the 3nd pass:

Y_{max} = 4E-06 t^2 – 0.004 t + 2.0001.

When hydrogen is introduced into the HHV chamber at the initial stages, palladium diffusion can occur faster, since hydrogen atoms encounter less resistance in the crystal lattice in the first layer, where the α-PdH_n alloy is formed, due to the relatively unfilled octahedral pores in the palladium lattice. However, with each subsequent saturation of α-PdH_n alloys, the internal stresses that arise and changes in the crystal lattice can slow down the hydrogen penetration process, increasing the time to reach the maximum. This is because with each new introduction, the hydrogen concentration in palladium increases and a temporary thermodynamically stable α-phase is formed for the Pd-H system. This can cause changes in the hydrogen absorption rate, since it takes more time to reach the same concentration at different pressures. Hydrogen accumulating in the palladium crystal lattice creates internal concentration stresses. With each new pass, these stresses can affect the mechanical properties of the material, as well as possible changes in the lattice structure caused by previous passes. Therefore, the maxima on the graphs are shifted to the right (to a later time).

Plateau: each new pass may require a different time to reach the equilibrium concentration of hydrogen in palladium. This may be due to a change in the thermodynamic conditions of the process of hydrogen penetration into the material due to previous passes. Therefore, after reaching the maximum bend, a plateau is formed on the curves for some time (Fig. 7), which signals the completion of the initial phase of rapid hydrogen penetration and the achievement of a certain equilibrium state, namely the thermo-baroelastic-diffusion state.

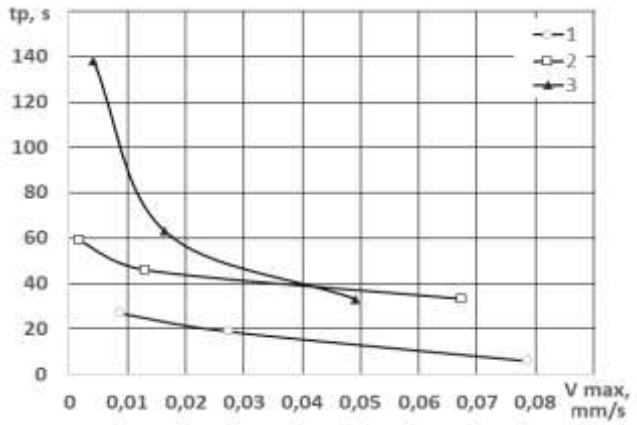

Fig. 7. Dependence of the plateau existence time during maximum bending on the speed of reaching the maximum bending according to the results of 3 experiments (Figs. 1–3) for three overhangs: 1 – for pure palladium; 2 – for the α-$PdH_{0.0077}$ alloy; 3 – for the α-$PdH_{0.0177}$ alloy

From Fig. 6, we can conclude that the speed of reaching the maximum affects the duration of the plateau: the longer the time to reach the maximum, the longer the plateau. Analyzing Fig. 6, we see that the plateau existence time during maximum bending for alloys with a higher hydrogen content increase, which also indicates the transformation of the initial material into a new material, and this is a process that continues in space and time. This process is implemented through the formation, development and functioning of a new temporary gradient metal-hydrogen alloy and the corresponding field of hydrogen concentration gradients. This leads to the appearance and growth of uncompensated macroscopic hydrogen concentration (HC) stresses (internal stresses of the first kind) in the plate, which cause the cantilever to bend. In the process of bending the cantilever, the internal stresses are reformed, which is accompanied by the redistribution of hydrogen (restructuring of the hydrogen concentration (HC) field) and, accordingly, the structure of the gradient alloy α-PdH_n is transformed and the internal conditions of hydrogen diffusion transport are adjusted. After hydrogen is introduced into the chamber, when gaseous hydrogen comes into contact with palladium in the near-surface layer, the concentration of dissolved hydrogen is almost immediately achieved (and subsequently maintained), which is practically equal to the equilibrium solubility of hydrogen at a given pressure and temperature. This leads to corresponding changes in the root cause of bending − the value of the hydrogen diffusion flux, which is initially determined by the hydrogen pressure and temperature. And then it is determined by the effective hydrogen diffusion

coefficient in palladium, which is much smaller than the true hydrogen diffusion coefficient in palladium (D * << D). Experimentally, we record this in the form of a plateau, which is a manifestation of thermo-baroelastic diffusion equilibria between elastically compressed and elastically stretched layers in the process of straightening the cantilever.

Such a study provides an understanding of the behavior of palladium when interacting with hydrogen and helps to evaluate the processes of saturation and expansion of the crystal lattice at the microlevel.

Relaxation: after the plateau phase, we see a decrease in bending on the graphs, which corresponds to the relaxation process – a slow decrease in internal stresses and the magnitude of bending for a cantilever made of α-PdH_n alloys due to the partial redistribution of hydrogen in the crystal lattice and stabilization of internal structural changes. This process is usually long and depends on the amount of hydrogen in the material and its kinetic features. With each subsequent hydrogen injection, the relaxation process also becomes longer, since more hydrogen accumulates in the material, and, accordingly, more time is required to stabilize the state. Stress relaxation, as can be seen from Figs. 1–4, also depends on the speed of reaching the maximum and the speed of reaching the set pressure and affects the straightening process and simultaneously on stress relaxation. At the same rate of hydrogen injection into the chamber, we observe an identical nature of the straightening kinetic curves.

Residual bending. The second stage of deformation at a temperature of 150 °C (see Figs. 1–4) is characterized by the existence of residual bending, which does not disappear during additional holding. It should be noted that with an increase in the hydrogen content in the α–PdH_n alloy, the magnitude of this bending increases. Therefore, during the saturation of the plate with hydrogen, the final equalization of the hydrogen concentration to the thermodynamic equilibrium state and the associated final straightening of the plate are not achieved, due to the establishment of a quasi-stationary thermo-baroelastic diffusion state and the field of residual elastic hydrogen-concentration stresses.

CONCLUSIONS

1. At a temperature of 150 °C, it was first established as a result of experimental studies that with the same increase in the hydrogen concentration in palladium (Δn=0.0084 H/Pd) in the α-$PdH_{0.0084}$ and α-$PdH_{0.0168}$ alloys, the time to reach the maximum bending (peak) increases for each subsequent pass. This indicates that the accumulation of hydrogen in the palladium structure causes changes in the kinetics of the hydrogen diffusion process and dilation of the crystal lattice of the material. The obtained data allow us to better understand the dynamics of hydrogen saturation of palladium at each stage of its saturation, which has not been studied in detail before.

2. For the first time, it was experimentally recorded that the shape of the curves, the rate of reaching a steady state, and the kinetics of the process of returning the cantilever to its initial state for α-PdH_n alloys depend on the rate of hydrogen introduction into the chamber and, accordingly, the rate of saturation and penetration of hydrogen into the interior of palladium.

3. It was experimentally established at a temperature of 150 °C that when the α-PdH_n alloy is saturated with an increase in the hydrogen content in the alloy, the residual bending of the cantilever increases and is from 16 to 33% relative to the maximum bending value.

4. It was experimentally shown that after reaching the maximum bending, a plateau is observed, which indicates the stabilization of the hydrogen penetration process, namely the establishment of a thermo-baro-elastic diffusion equilibrium in palladium, which signals an equilibrium state between hydrogen penetration and the mechanical response of the α-PdH_n alloy. This plateau is important for understanding the limiting level of hydrogen saturation of palladium and its effect on the crystal lattice, which has not been clearly recorded before.

5. The study showed that the duration of the relaxation process of hydrogen concentration stresses after each injection increases with increasing hydrogen content, which was first recorded on the basis of direct experimental data when the concentration change occurs by the same amount (Δn=0.009 H/Pd) for the α-PdH_n alloy.

6. The results of the experiment at a temperature of 150˚C show that for the α-PdH_n alloy, the maximum cantilever bending decreases with the same increase in hydrogen concentration with each subsequent injection of hydrogen into the chamber. This fact can be explained by the gradual saturation of the crystal lattice of the α-PdH_n alloy and partial deformation stabilization, which requires further study to fully understand the behavior of hydrogen in solids. This opens up new prospects for predicting the mechanical properties of materials used in environments with a high hydrogen content.

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ДОСЛІДЖЕННЯ ПРОЦЕСУ ВЗАЄМОДІЇ СПЛАВУ ПАЛАДІЮ З ВОДНЕМ В α-`ОБЛАСТІ ДІАГРАМИ Pd-H

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Проведено дослідження впливу швидкості подачі водню в камеру на процес формозмінення кантилевера з чистого паладію і сплаву α-PdH_n при температурі 150 °С. Показано, що процес насичення паладію воднем відбувається у два етапи: швидке згинання, досягнення максимального вигину з утворенням плато, та поступове розпрямлення кантилевера до стаціонарного стану. Встановлено, що швидкість подачі водню в камеру впливає на кінетику процесу формозмінення кантилевера та на швидкість досягнення стаціонарного стану.