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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 study of the influence of the hydrogen supply rate into the chamber on the deformation process of a cantilever made of pure palladium and α-PdHn alloy at a temperature of 150˚C was conducted. It was shown that the process of palladium saturation with hydrogen 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 with the presence of residual bending. It has been established that the rate of introduction and, accordingly, the rate of saturation and penetration of hydrogen into the palladium lattice affects 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-PdHn alloys.

Palladium is a platinum group metal known for its high hydrogen absorption capacity. It has a cubic face-centered crystal structure with a lattice parameter of 3.889 Å [1]. Hydrogen penetrates into the octahedral cavities of the palladium crystal lattice, causing its expansion. In the α-phase, hydrogen atoms occupy the octahedral cavities, which leads to a slight lattice expansion to 3.91 Å, and in the β-phase, the lattice parameter can reach 4.025…4.06 Å. The transition between the phases depends on the hydrogen concentration and temperature.

An advanced hydrogen-vacuum unit (HVU) was used to conduct the experiments [2]. The samples, made in the form of cantilevers (plates measuring 68 × 5.5 × 0.27 mm of palladium with a purity of 99.9 %), were coated with a 750 nm thick layer of copper, which is impervious to hydrogen, using an electrolytic method [3]. After that, the samples were heated in the HWU chamber to the experimental temperature (273K+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-PdHn 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 in isothermal conditions to relieve concentration stresses, after which additional one-sided saturation of cantilever to α-PdHn alloy was performed, where n changes for each alloy by the same value. The process of shape change was recorded using a catheter and recorded on a video camera. Then the results were decoded and time dependencies of the cantilever shape change during the saturation process were plotted.

A series of experiments was performed for cantilevers made of α-PdHn alloy, where $n_{i+1} = n_i + \Delta n$ varies for each alloy depending on the hydrogen pressure in the chamber (Fig. 1). A series of experiments were conducted where the concentration was changed to Δn = n, Δn = 1.3n, and Δn = 1.1n, respectively.

Fig. 1 shows that the saturation process of cantilever from pure palladium and from the α-PdHn 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 start of hydrogen supply to the chamber of the hydrogen-vacuum unit.

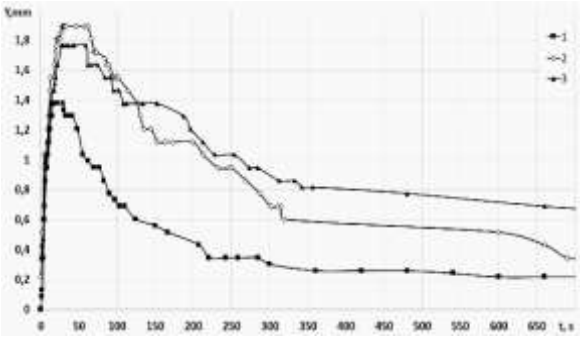

Fig. 1. Time dependences of cantilever shape change 1 – for pure palladium; 2 – for α-$PdH_{0.0077}$ alloy; 3 – for α-$PdH_{0.0177}$ alloy at a hydrogen injection rate of 0.01 MPa/s

At the same time, when the appropriate pressure (P) is reached on the manometer during the time (Δts, 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 the maximum value (Ymax, mm), and then a plateau with a duration of (tp, s) of several seconds is observed, and then a second longer stage of cantilever straightening begins with the achievement of a stationary state (Yst, mm) in a certain time (Δtst, s), which does not change during additional exposure.

Let us consider in more detail one of the experiments (see Fig. 1, Curve 2), when the saturation of 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 bending of the cantilever continues to increase and reaches its maximum value of Ymax = 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 the curved maximum position. Then the cantilever 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 steady state (Yst = 0.34 mm), which does not change during a further long exposure of 810 s.

Interestingly, if we increase the pressure in the chamber from 0.036 to 0.061 MPa at $\Delta\tau s = 2.5$ s, and create an α-PdH0.0264 alloy when the concentration changes by $\Delta n = 0.0087$, which is a smaller value than in the previous experiment, we experimentally recorded a smaller maximum bending of the cantilever (Umax = 1.77 mm) at $\Delta\tau max = 36$ s (see 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 ($\Delta t = 0.51$ mm) after 1200 s. Additional exposure for 3600 s did not lead to a change in the position of the cantilever.

Analyzing curves 1, 2, 3 in Fig. 1, we can note that all curves have a similar shape, which indicates a similar mechanism of hydrogen absorption, 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 a plateau in Fig. 1, lasting 10, 33, 33 s, respectively, for each experiment. This plateau indicates the establishment of a thermo-baroelastic-diffusion 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-PdHn 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 obtained results should be clarified and analyzed from two more angles, when the hydrogen concentration in palladium changes by the same amount for different alloys and the rate of hydrogen injection into the HVU 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 rate of hydrogen supply to the chamber for the alloys listed in Fig. 2. 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 Fig. 2.

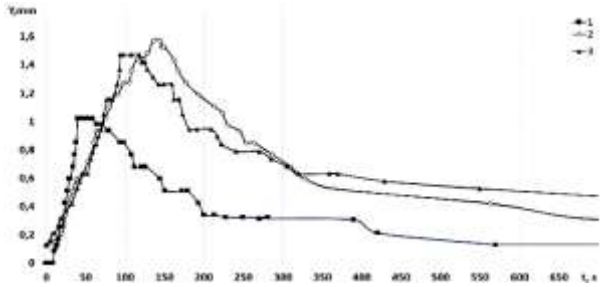

Fig. 2. Time dependence of cantilever deformation 1 – for pure palladium, 2 – for α-PdH0.0077 alloy, 3 – for α-PdH0.0177 alloy at a hydrogen injection rate of 0.0002 MPa/s

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, 2, 3). Then, for each experiment, we record the presence of a plateau of different duration – 19, 12, 24 s, which indicates the establishment of a quasi-thermal-baroelastic equilibrium and a change in the nature of the cantilever saturation process and the redistribution of internal stresses. 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 from 94 to 98 s for curve 1 the establishment of the 2nd plateau, which is mirrored in curve 3 from 142 to 159 s. Then the straightening process 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 is slow 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, which increase over time, 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 we can see, 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. Next, we observe a gradual decrease in the maximum bend, but the kinetics of the process differs from curves 1 and 3: there is no plateau and the straightening process is quite smooth.

To confirm the fact that the speed affects the nature of the cantilever straightening curve after reaching the maximum bend, we conducted an experiment when the feed rate was reduced by almost 200 times compared to experiment 1 (Fig. 3). The temperature and pressure of the experiment were left unchanged, and the results of the experiment were recorded.

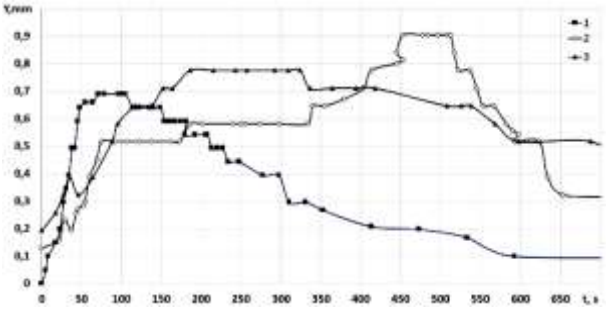

Fig. 3. Time dependences of cantilever shape change 1 – for pure palladium; 2 -– for α-PdH0.0077 alloy; 3 – for α-PdH0.0177 alloy at a hydrogen injection rate of $4.8 \cdot 10^{-5}$ MPa/s

Fig. 3 shows that when the rate of hydrogen supply to the chamber changes almost 200 times compared to experiment 1, 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 s, 484 s, and 186 s (see Fig. 3, curves 1–3, respectively) and is accompanied by the formation of a long-lasting 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 begins to gradually 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 occurred at almost the same rate of about $4.9 \cdot 10^{-5}$ MPa/s and the kinetics of straightening is very similar, unlike curve 2, where the injection rate was less than $5.3 \cdot 10^{-5}$ MPa/s. Here, 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 characterized 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 the 3rd curve, after 1600 s, the residual bending is 33% of the maximum bending and during 780 s of additional exposure is also unchanged.

Therefore, it can be concluded that the hydrogen supply rate during saturation of pure palladium (see Fig. 3, curve 1) and its α-PdHn alloy (see Fig. 3, curves 2 and 3) affects the magnitude, time of reaching 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 infusion, 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 Fig. 4.

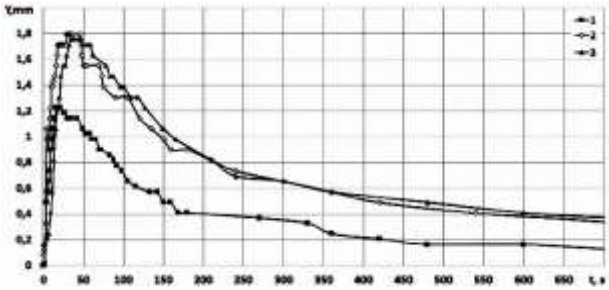

Fig. 4. Time dependences of cantilever shape change 1 – for pure palladium; 2 – for α-PdH0.0084 alloy; 3 – for α-PdH0.0168 alloy when the concentration changes by 0.0084H/Pd and the hydrogen injection rate into the chamber is 0.01…0.007 MPa/s

As we can see (see Fig. 4), a change in the hydrogen concentration by the same amount 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 = 0.084 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 seconds, the curves show a rapid increase in the bending of the cantilever 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; 11 s, 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 at 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 an increase in the hydrogen content in the alloy, the residual deformation increases and amounts to 6, 9, and 18% (respectively for curves 1, 2, and 3, Fig. 4) relative to the maximum bend. In Fig. 4, curves 2 and 3 correspond to the experiment with a hydrogen supply rate of 0.0065 MPa/s to the installation 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 a 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 characterized by curve 1 (see Fig. 4).

Let's look at the behavior of the curves in Figs. 1-4. Maximum bending (peaks): each graph has a pronounced maximum bending after the initial period of hydrogen saturation. This maximum corresponds to the moment when the hydrogen concentration in palladium reaches a value that causes maximum strain due to the expansion of the crystal lattice. Although the concentration changes by the same amount with each infusion, the maxima appear at different times, which is influenced by the rate of hydrogen supply to the chamber.

Plateau: Each new infusion may require a different time to reach the equilibrium hydrogen concentration 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 infusions. Therefore, after reaching the maximum bend, a plateau is formed on the curves for some time, which signals the end of the initial phase of rapid hydrogen penetration and the achievement of a certain equilibrium state, namely the thermo-baro-elastic diffusion state. The speed of reaching the maximum affects the duration of the plateau: the longer the time to reach the maximum, the longer the plateau.

Relaxation: after the plateau phase, the graphs show a decrease in bending, which corresponds to the relaxation process slow decrease in internal stresses and bending for cantilevers made of α-PdH_n alloys due to partial redistribution of hydrogen in the crystal lattice and stabilization of internal structural changes. At the same rate of hydrogen injection into the chamber, we observe an identical character of the kinetic straightening curves.

Residual bending. The second stage of deformation at a temperature of 150 °C (see Fig. 1-4) is characterized by the existence of residual bending, which does not disappear during additional exposure. It should be noted that with an increase in the hydrogen content in the α-PdHn alloy, the magnitude of this bend increases. Therefore, during the saturation of the plate with hydrogen, the final equalization of the hydrogen concentration to the thermodynamically 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, for the first time, as a result of experimental studies, it was found that with the same increase in the hydrogen concentration in palladium (Δn = 0.084 H/Pd) in the alloys α-PdH0.0084 and α-PdH0.0168, the time to reach the maximum bend (peak) increases for each subsequent infusion.

2. For the first time, it has been experimentally documented that the shape of the curves, the rate of reaching the steady state, and the kinetics of the process of returning the cantilever to its initial state for α-PdHn alloys depend on the rate of hydrogen injection into the chamber and, accordingly, the rate of saturation and penetration of hydrogen into the middle of palladium.

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

4. The study showed that the duration of the process of relaxation of hydrogen concentration stresses after each infusion increases with the increase in the amount of hydrogen, which was first recorded on the basis of direct experimental data.

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