Peculiarities of structural changes in Pd and Pd-alloys.

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It has been discovered that kinetics of structural changes in Pd and Pd-alloys under the influence of dissolved hydrogen seems to be non-trivial. As a rule, structural changes in these systems include correlation changes of co-existing phases concentration and the defect structure character. These changes have the stage character. Basic stages are: incubation period, quick degassing, temporal stabilization and post-stabilization period. The structural changes and phase transformation in Pd-M-H kinetics happens to be non-monotonous (oscillating or stochastic). Such time dependence can be observed during tens thousand hours. The hypothesis based on the ideas of non-equilibrium dynamics and specific attributes of hydrogen interaction with matrix defect and atoms in Pd-systems has been offered in order to explain discovered phenomena.

I. INTRODUCTION

Unique ability of palladium for big quantity of hydrogen dissolving was discovered about 130 years ago by Graham [1], the one of most known UK chemists. The dissolving of H in Pd considerably has influence over physical properties [2,5]. The Pd-H alloy is diamagnetic and super conductive though Pd is strongly paramagnetic. These differences are connected with the atomic and electronic structural changes at H dissolving in Pd. Here only atomic structure characteristics will be considered. Solid solutions of H in Pd create α - phase if H concentration (this values are described as n_H/n_Pd where n_H and n_Pd are quantities of H and Pd atoms, respectively) is not more than 0.02-0.03 or β - phase if H concentration is more than 0.6. If H concentration is between those values mix of these phases appears. In both phases Pd - atoms create fcc-structure, where H - atoms are in octapores. Distance between Pd - atoms in β - phase exceeds corresponding distance in α - phase on 3%. That is why α ↔ β phase conversions processes are followed by the defect generation. Structural changes taking place in Pd - H during the saturation and following degassing have become an object of systematic researching very recently. The results of the researching of α - and β - phases peculiarities changes of shares relations and defect structures forming during α → β (during saturation) and during β → α (during degassing) processes were the most interesting. These processes including their kinetics have been fully discovered in the cycle of our researching [4 - 12].

Non-ordinary data received in these researching showed the important role of defect structure forming (at saturation) and transforming (during degassing). That is why the character of hydrogen influence on structural changes in Pd - H solutions and their kinetics were very interesting. Disordered mutual Pd and M atoms distribution is the source of the additional defect structure formation comparing to Pd. The brightest effects should be expected in those solutions that are different from Pd by the degree of affinity to hydrogen. It could lead to some new characteristics of structural changes in palladium systems appearance under the influence of the saturated hydrogen. The results of the researching [13-16] confirmed that the structural changes in palladium solutions have non-trivial character.

The purpose of this paper is to consider Pd and some Pd-M solutions structural changes characteristics at the saturation and following degassing. The researching was led by X-rays methods that are described in detail in [4-16].

The hydrogen saturation has been led by electro-chemical method at the current density 2.5-80mA/sq. sm and the saturation time was 7-120min. The samples degassing going spontaneously while kept at the open air leads to spontaneous structural changes in the samples saturated by hydrogen.

Researched samples were the plates with the thickness of 0.1-2mm, whose surfaces were polished and ground. The deformation effects in some samples were taken off by the annealing. The saturation was led either by one act or by some acts of repeating cycles ‘saturation-degassing’ (cycling).

II. THE PECULIARITIES OF PHASE TRANSFORMATION IN PD-H.

Let’s take a look at the curves of the β-phase concentration p(t) dependence on the saturation time at low current density (2.5mA/sq.sm). Fig. 1 shows the dependence of ln[p(t)] function on the saturation time. Curves 1,2,3 relate to such blocks of coherent scattering (further - hkl-blocks), whose crystallographic plains with (100), (311), (110)

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indexes, respectively, are parallel to external surface of the sample. Fig.1 shows also that the experimental points lay on the straight lines that do not go through the coordinates beginning.

Received data shows the dependence of $\beta$ - phase concentration on time, which is

$$p(t) = 1 - \exp[-\gamma(t - t_0)]$$

(1)

Here $\gamma$ is logarithmic velocity of $\beta$ - phase quantity growth, $t_0$ - the incubation period duration. The logarithmic velocity of the growth and the incubation period duration depend on crystallographic orientation of block plains relatively to external surface. $\gamma$ reaches its maximum at (100) blocks and minimum at (110) blocks, $t_0$, on the contrary, reaches its minimum at (100) blocks and its maximum at (110) blocks. The orientation dependence considered to be stronger for $\gamma$ value than for $t_0$'s. Besides $t_0$ and $\gamma$ seemed to depend on current density $j$ essentially. At $j$ increasing up to 25mA/sq.cm $t_0$ becomes almost 40 times less for (100) blocks, $\gamma$ becomes one order more.

This data could be explained basing on the phase transformation of 1st order [7] kinetics theory. According to this theory phase transformation from $\beta$- to $\alpha$ - phase takes place then the decreasing of volume energy connected to creating of new phase exceeds energy loss which has gone for appearance of boundaries between new phase and old one, defect generation, increasing of matrix elastic energy connected to elastic tension appearance because of specific volume phase difference. During $\alpha \to \beta$ - transformation effective pressure of saturating hydrogen, defined by current density in electrolytic bath is included in thermodynamic stimulus. The embryos of new phase at $\alpha \leftrightarrow \beta$ transformation have the plate form. That is why energetic loss connected to elastic tension in matrix because of the inbuilding there of the new embryos has an anisotropy . Elastic energy of this kind of embryos appearing reaches minimum if their surfaces are parallel to the crystallographic plains kind of (100).

Defect structure has an influence over thermodynamic stimulus of phase transformations and kinetics of this transformation. It has been shown experimentally that the phase transformation takes place by the way of spontaneous moving of the boundary between $\alpha$ and $\beta$ - phases. Because of that the velocity of $\beta$ - phase concentration increasing depends on energetic barriers value, which have to be got over during this boundary migration on the potential relief of $\alpha$ -phase crystal. The defects leading to non-regularly distributed energetic barriers of different highness hamper the board moving and decreasing of $\alpha \to \beta$ transformation velocity . The energy of inter-phase boundary migration reaches its minimum if the embryo surface is parallel to the crystallographic plains kind of (100).

Specified factors explain the existence of the incubation period and its anisotropy, decreasing $t_0$ at the $j$ increasing and its increasing at the defect concentration increasing, stronger anisotropy of new phase growth velocity.

Let us consider the peculiarity of the structural changes during $\beta \leftrightarrow \alpha$ transformation. The researching was led after one-act saturation of annealed and deformed samples and annealed samples saturated by a few cycles.

The $\beta \to \alpha$ transformation in one act saturated ($j=40mA$/sq.cm, $t_{\text{sat}}=15\text{min}$) annealed sample had started right away after the saturation, during first 25 hours the $\beta$- phase contains became 30 times less. First 5 hours had been an incubation period in deformed sample. The $\beta$-phase concentration had became 2.5 times less during next 25 hours . During next 150 hours it had decreased to 30 % from the original value.

The $\beta$ - phase concentration changing at cycle saturation of annealed sample is showed by Fig. 2 and 3 [6,11]. Fig. 2 shows that the incubation period is absent during first three cycles. The degassing velocity is decreasing while the number of cycles is increasing. The incubation period appears after fourth saturation. The curves of dependence of the $\beta$-phase concentration after ninth saturation are showed on Fig. 3. Right after this saturation $p(t)$ was 90%. This value stays unchangeable during 4 thousand hours. After that the $\beta$ -phase concentration was decreasing during 46 thousand hours. Then the concentration of this phase stopped changing. This stop was fixed during 50 thousand hours. After that the $p(t)$ changing which has oscillating character starts again.

Therefore, $\beta \to \alpha$ process has the stage character. Unlike the $\alpha \to \beta$ process, the $\beta \to \alpha$ transformation takes place spontaneously while kept at open air. Its initial stage is hampered by original defect structure. Further process developing is specified by new defect generation and following defect structure transformation.

Regarding to it the incubation period was noticed after one-act saturation only in deformed sample. Starting after fourth saturation it was noticed in annealed sample. After ninth saturation its duration was much longer than after the mechanical treatment applied to surface because the density of dislocations is essentially bigger .

The $p(t)$ decreasing during next stage of degassing corresponds to the exponential characteristics only at the defect concentration which is not big. The increasing of this concentration and the creating of complexes (vacation complexes, dislocation walls) following it, leads to appearance of wider and higher energetic barriers in a space. It provides, regarding to [8], its transition to power and even to logarithmic dependence of $p(t)$ decreasing. The transition to the next stage where $p(t)$ stops changing is caused by specific transformation of defect structure. One of its characteristics is blocks growth in $\alpha$-phase [1], which takes place because of dislocation walls migration to blocks boundaries. Because this process happens in different parts of sample with different velocities, the additional non-regularity appears in the system in distribution of energetic barriers on potential relief of the $\alpha$-phase crystals. This leads to additional
Found non-ordinary kinetics of structural changes in Pd-H caused by defect structure transformation had stimulated the structural changes kinetics researching in Pd-M-H alloys.

The kinetics aspects of those changes were being researched on Pd alloys with W[13-14], Sm[15], Er[16-21] and, besides, the most in detail on annealed Pd-W (11.3 at% W) and deformed Pd-Er (8at%Er). The ingredients of those alloys are essentially distinguished by the degree of the affinity to hydrogen and, besides, W’s affinity to hydrogen is lower than Pd’s and Er has higher one than Pd does. Regarding to the diagrams of equilibrium for these alloys, β-phase does not appear. Pd-W alloy (11.3at%W) in accordance to [23] is characterized by the appearance of regions rich in W, that sizes are 2-3nm and superfluous concentration of vacancies [24]. Pd-Er alloys (8at%Er) is close to the solubility boundary.

Let us take a look at the experimental data for Pd-W alloys. Fig. 4 shows the dependence of $ln(I_{400}/I_{200})$ on time after third saturation (here $I_{400}$ and $I_{200}$ are normalized intensities of the diffraction maximums (400) and (200))[13-14]. This dependence seems to be quasi-periodic. Its character shows that the oscillation processes of two types take place in the system. One of them is connected to the structural changes causing the quasi-periodic changes of $ln(I_{400}/I_{200})$ function. On the initial stage those oscillation have a period of 7 days approximately. The second one is connected to the structure changes that are characterized by abrupt short-term enbroadings of diffraction maximums and decreasing of their top parts, that happen every 4-5 weeks (the enbroaded diffraction maximums ‘wings’ expand so far that their proper measurements are unlikely possible). Quasi periodic structural changes of 1-st type transform to the stochastic ones after system’s transition through the structural change of 2-nd type.

The $ln(I_{400}/I_{200})$ function decreasing for the first of those processes can be caused by the appearance of defect regions that sizes are 2-3 nm[25]. Those regions differ from the matrix by the specific volume. The increasing of function can be connected either to dissolving of those regions or to the approaching of their specific volume to the matrix’s one (their disappearance as defect ones). The width oscillations of diffraction maxima can be connected to appearance and following disintegration of dislocation loops that sizes are 5-10nm[25].

The oscillation structural changes appearance after the hydrogen saturation of the system indicates the clusters rich in hydrogen formation in the matrix rich in Pd. The specific volume of these clusters is bigger than matrix’s and because of it they are not stable in thermodynamics meaning in normal conditions. For the non-contradictory model of this phenomenon construction one should suppose that the non-stability decreasing would take place in account of its defect degree decreasing because of the diffusion of the superfluous vacancies being in this alloy into clusters enriched by hydrogen. Vacancies deficit arising during this process in the regions rich in W will be stimulated by the contra-directed vacancies diffusion. The consequence of it will be the oscillation process of vacancies moving that will lead to the structural oscillation of 1-st type. After a few periods the concentration of vacancies in regions rich in palladium become so high that it seems more profitable to form large vacancies dislocation’s loops during the intermediate period. But those loops are not stable. Soon after their arising they disintegrate, after that the process of defect clusters formation and disappearance renews. The offered model is, of course, hypothesis and needs more direct proves. Nevertheless, it describes experimental data and, undoubtedly, can be the base of stricter model for the found phenomenon researching.

The initial condition of deformed by grinding and polishing Pd-8%atEr alloy is characterized by essentially non-homogeneous distribution of the ingredients and availability of strong enough stretching tension which is perpendicular to the surface. After the hydrogen saturation this tension transformed to compression tension as strong as it was. Maximum compression tension reaches in 2 days after the hydrogen saturation. After 8 days its value has become 25% less, after that it stays practically the same during 1.5 years of the observation[17-18].

The form of the diffraction maxima had changed after the saturation. They became doublets (fig.5). This indicates the arising of two phases that essentially differ from each other by the period of lattice in considered system. One may see that the profiles of maxima dependence on time has oscillating character (fig.6). The computer analysis of those profiles lets us determine the time dependencies of differences in concentrations of erbium in corresponding phases and specific portions of those phases. The data presented on the fig.7 shows that non-regular oscillating (stochastic) changes of the indicated characteristics have been taking place for 1.5 years. These oscillations happen on the initial
stage of degassing when there is 10-20% of H in the system and on the later stages when the concentration of H is not more than 1%.

For the received data explaining the model taking into consideration the idea of microscopic theory of alloys and synergetic has been elaborated. The lattice compression which has been found after the saturation can be caused by the transformation of defect-metal (DM) complexes being in alloy before the saturation into hydrogen-defect-metal (HDM) complexes because of the bigger energy of hydrogen -defect bond in Pd[26]. Therefore, the last complexes have low specific volume. These complexes because of high erbium’s affinity to hydrogen attract erbium atoms and become traps for erbium. These traps play mutual role. They keep the system in non-equilibrium condition and lead to rising diffusion appearance. According to synergetic conception, non-equilibrium condition of the system admits the appearance of the oscillating processes [27] connected to self-organization of defect-structural states. The competition of rising and gradient diffusions present the mechanism allowing possible oscillating processes to be realized. The diffusion fluxes multitude caused by this competition in two-phase system containing the Er traps leads to oscillating character of the phase transformation kinetics. The stochastic character of those oscillations is connected to the essential difference of the relaxation time of different oscillating processes in considered system.

IV. CONCLUSION.

Therefore, the structural changes peculiarities in hydrogen-containing systems Pd-H and Pd-M-H, whose M-ingredients essentially differ from each other by the degree of affinity to hydrogen were considered in this paper. Non-trivial kinetics of $\beta \rightarrow \alpha$ transformation has been found for Pd-H. The most important its peculiarity is the alternation of the stages where the $\beta$-phase concentration changing happens or does not happen. This phenomenon is connected to the influence of as original defect structure as its transformation during the procces of phase transformation over $\beta \rightarrow \alpha$ transformation kinetics. The second important $\alpha \leftrightarrow \beta$ transformation peculiarity is strong dependence of the p(t) function on (hkl)-blocks orientation relatively its external surface. It caused by the elastic energy dependence evoked by the plate formation, on its orientation in the blocks.

The structural changes kinetics in Pd-M-H has an oscillating character. This kinetics peculiarities are connected to the defect subsystem caused by non- homogeneous distribution of the metal ingredients and ,as a result, by hydrogen non-homogeneous distribution. Hydrogen is being captured by regions that have high energy of the bond to hydrogen that keeps the system in non-equilibrium state. This leads to diffusion fluxes multitude where arising and gradient diffusion are competing. As a result, 'static' non-stability transforms into dynamics one similar to Benard's cells [27]. According to real alloy structure the oscillation character of the structural changes can acquire different characters. The structural changes are the defect regions appearance and disappearance alternation in Pd-W-H. The structural changes have the form of phase transformations of stochastic type in Pd-Er-H.

The long-term oscillating structural changes in hydrogen-containing alloys correlate with the similar strength characteristics changes; for example roll steel [28]. That is why actual direction of further investigations is founding of such metallic alloys for that this phenomenon is observed, researching of their nature and their practical use possibility.

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FIG. 1. Logarithmic dependence of $\beta$-phase concentration $p$ on time after the hydrogen saturation for hkl-blocks: 1-(100), 2-(311), 3-(110)
FIG. 2. $\beta$-phase concentration dependence on time for cycles from first to fourth: 1, 2, 3 and 4 are cycles numbers, the arrows show the p changing at hydrogen saturation.

FIG. 3. $\beta$-phase concentration dependence on time after ninth hydrogen saturation for (100) and (311) blocks; incubation period is omitted.
FIG. 4. $\ln(I_{400}/I_{200})$ dependence on relaxation time for Pd-11.3at% W alloy after the third hydrogen saturation

FIG. 5. The profiles of diffraction maximum for Pd-8at%Er alloy 20 min, 130 min, 330 min and 1300 min after the hydrogen saturation
FIG. 6. The profiles of diffraction maximum for Pd-8at% Er alloy 1.5 hours (1), 7 hours (2), 25 hours (3), 48 hours (4), 120 hours (5), 4200 hours (6) after the hydrogen saturation

FIG. 7. Phase rich in Er concentration dependence on time for Pd-8at% Er after the hydrogen saturation