

FEATURES OF PHASE TRANSFORMATIONS IN THE FOILS OF ALLOY Pd-8,3at.%Y-H DURING RELAXATION

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Introduction

The unique ability of the alloys on the basis of palladium, to pass with the high speed a large quantity of hydrogen, led to the wide use of these alloys in the industry as the membranes for purification of hydrogen. In this case arose the need of a study of operating characteristics of the membranes, since under the action of hydrogen can change not only dislocation structure, but also the redistribution of atoms, up to the phase transformations.

At present for the preparation of high-purity hydrogen from gas mixture some of the promising are the alloys of palladium with the rare-earth metals, namely, the system Pd-Y, whose ability to absorb hydrogen in a certain interval of yttrium concentrations is 2-3 times higher than in the alloys of system Pd-Ag and Bi, used in industry at present. Furthermore, the alloying of palladium with yttrium atoms increases the strength characteristics of alloys, as a result of which should be expected an increase in the operating life. However, in the systems Pd-Y after hydrogen saturation during long-term relaxation phase transformations can occur, since the large number of vacancies, which enter the matrix of alloy during the hydrogenation, and the large number of hydrogen atoms increases the diffusion mobility of the atoms of components in these systems.

This work is dedicated to the study of the nature of phase transformations observed in the Pd-8,3 at.%Y alloy in the form of foil 130 μm thick after threefold hydrogen saturation during long-term relaxation by the X-ray diffraction analysis.

Results and consideration

For the first time in alloy Pd-8,3at.%Y, located at a temperature hydrogen saturation near the two-phase region during long-term relaxation under normal conditions after hydrogenation, observed phase transformations. In Fig.1 are represented the diffraction patterns of line (200) of the studied alloy after electrolytic hydrogenation for the different relaxation time.

As we have established earlier, hydrogen saturation of palladium and alloys on its basis leads to the formation of a large quantity of vacancies, and, therefore, also to an increase the diffusion

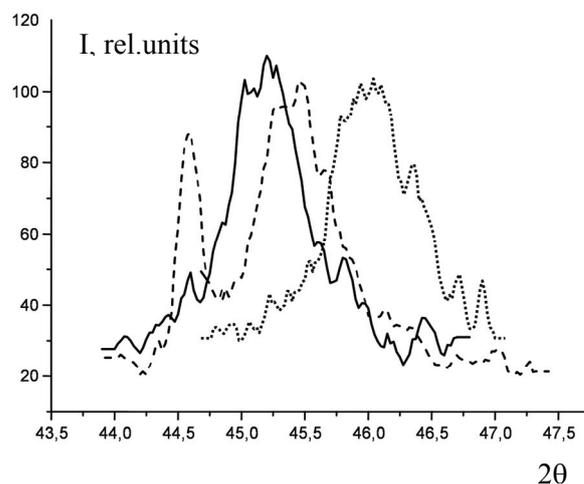


Fig.1. X-Ray diffraction maximum (200) for the different relaxation time:

..... – as-prepared state; ——— - 1 h after the third saturation; - - - - - 840 h after the third saturation.

constant of the components of alloy. Because of this during 850 h. at room temperature the alloy Pd-8,3at.%Y is decomposed into three phases: enriched hydrogen phase Pd₇Y-H, α -solid solution Pd-8at.%Y-H and the phase, in which yttrium concentration is reduced to 4 at%. It is evident from fig.1 that the state of 840 hours of relaxation is characterized by the presence of a large quantity of hydrogen, since the diffraction line, which relates to this state, is located substantially to the left, than in the as-prepared state.

Further increase in the relaxation time led to the fact that hydrogen leaves from the basic phase. So in the period 8400-13700 h. of relaxation the hydrogen content $n_{\text{H}}/n_{\text{Pd-Y}}$ is 0,04 only. It is obvious that hydrogen must leave, also, the phase Pd₇Y, but the period of the lattice of this phase calculated from the experiment even grows. A similar result means that the peak, correspond to smaller diffraction angles, belong to the phase Pd₃Y, in which practically there is no hydrogen. By the additional confirmation of this is the fact that the width of this peak for all states less than the width of basic peak, and it decreases almost twice with an increase in the relaxation time from 8400 to 13700 h. (Fig.2). The peak corresponding to the larger diffraction angle we identified as the phase, depleted by yttrium. After calculating the

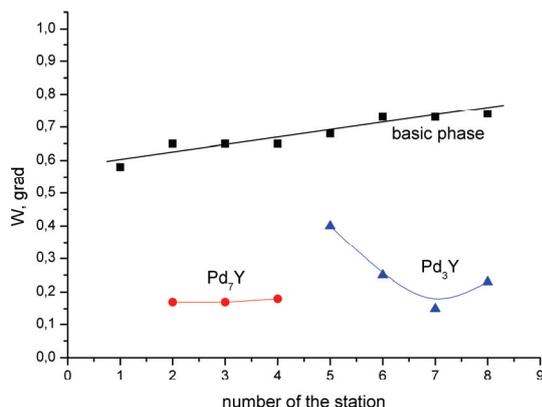


Fig.2. Dependence of the angular half-width of diffraction line on the relaxation time.

period of the lattice of this phase, it was established that the yttrium content is 4 at%, hydrogen content - 0,12. Since hydrogen leaves first of all the regions, depleted by yttrium (in the form of its larger affinity with yttrium atoms, than with palladium atoms), decrease of the period of the phase, observed to the right of basic peak, indicate of reduction in yttrium concentration in it during long-term relaxation. So after 13000 h. relaxation, calculated period of the lattice of this phase became less than the period of the lattice of pure palladium. The obtained result can be explained by the fact that yttrium atoms left this phase as a result of phase transformations, whereas high concentration of vacancies was formed. Calculations showed that it reaches 6%.

Conclusions

Conducting for a long time the regular X-ray diffraction studies of foils of the alloy Pd-8.3at.%Y after their electrolytic hydrogenation makes it possible to formulate the following results.

□ With the high content of hydrogen and vacancies in the matrix of the alloy the solid solution Pd-8,3at.%Y is decomposed into the phase Pd₇Y-H and α -solid solution Pd-8at.%Y-H. A quantity of hydrogen in the superstructural phase is higher than in the phase Pd-8at.%Y-H.

□ On leaving hydrogen from the phase Pd₇Y-H during relaxation, it is decomposed, and Pd₃Y is formed (but in a considerably smaller quantity). Phase Pd₃Y does not contain hydrogen.

□ The irregular distribution of yttrium atoms in the as-prepared alloy contributes to irregular distribution of hydrogen atoms in the matrix after hydrogenation to. This is due to the fact that yttrium has a larger affinity with hydrogen, than palladium.

□ The solubility of hydrogen in the alloys Pd-Y-H is determined not only by the concentration of yttrium atoms, but also by the

defective state of the alloy before saturation. In this case should be advised, that the defective state of sample can change both in the process of saturation itself and in the process of relaxation.

□ It is established that the phase, depleted by yttrium, contains about 6 at.% of vacancies.

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References

1. Revkevich G.P., Mitkova M.M., Katsnelson A.A. // Vestn. Mosk. Univ., Ser.3, 38 (4), 27, (1997).
2. Avdyukhina V.M., Revkevich G.P., Nazmutdinov A.Z., Burhanov G.S., Roshan N.R., Kol'chugina N.B. // Poverhnost. Rentgenovskie, sinhrotronnye i neitronnye issledovaniya, (10), 9, (2007).
3. Burhanov G.S., Gorina N.B., Kol'chugina N.B., Roshan N.R. // Ros. Khim. Zh., L (4), 36, (2006).
4. Sakamoto Y., Takao K., Flanagan T.V. // J. Phys. Cond. Matter., 6, 2321, (1994).
5. Takao K., Sakomoto Y., Yoshido M. // J. Less-Common Metals, (152), 115, (1989).
6. Fukay Y. // J. Alloys and Comp., 321, 195, (2001).
7. Doule V.L., Harris I.R. // Platinum Metals Review, 32, (3), 130, (1988).
8. Revkevich G.P., Olemskoy A.I., Katsnelson A.A., Mitkova M.M. // Vestn. Mosk. Univ, Ser.3, 33, (2), 74, (1992).