Hydrogen induced structural damages of palladium membranes and reliabilities of its exploitation during extra pure hydrogen production

G. I. Zhirov[1], M. V. Goltsova[2], V. A. Goltsov[3]
Donetsk National Technical University, Donetsk, Ukraine
E-mail: Goltsova@fem.dgtu.donetsk.ua
1 – Assistant Professor of Physics Department, DonNTU,
2 – Ph.D., Associated Professor of Nonferrous Metals and Constructional Materials Department, DonNTU,
3 – Doctor of Science, Full Professor, Head of Physics Department, DonNTU

Technology and apparatuses for extra pure hydrogen production with palladium membranes were elaborated in 1950–1960, firstly because of semi-conductors elaboration and production. Further hydrogen-membrane technology was defined as very effective for hydrogen-containing industrial gases separation. So, it is important for chemistry and petrochemistry, mineral fertilizers production, ferrous and non-ferrous metals industry, for feeding, purifying and separating hydrogen isotopes in thermonuclear reactors, for hydrogen energy tasks solving.

A vulnerability of hydrogen membrane technology is a deficient reliability of palladium membranes and its destruction under hydrogen influence. Due to this, an actual problem is to study hydrogen induced structural transformation in palladium and palladium-hydrogen alloys. This metal-physic and technological direction of development of hydrogen producing with membrane method is carried out in Donetsk National Technical University.

In the present work the results of structural damages studying during non-equilibrium hydrogen loading (hydrogen "impacts") are represented.

A material for research was a pure palladium (99,98%) as a wire of 0.5 mm diameter. Samples of 23 mm length were firstly bended in form of П. Than the samples were annealed in vacuum at 1000°C during 1 hour. An average size of grain after annealing was of 0.45–2.6 mm. Then samples were put into the working chamber of special hydrogen-vacuum device HVD-2, which realizes 2 research techniques simultaneously on one sample. First is electrical resistance measuring and the second is optical microscopy in situ with videorecording processes taking place in samples subsurface layers. The latter is extremely important for rapid processes.

So, there were registered following structural damages.

The reverse stationary swelling.Samples were put into the working chamber of HVD-2, and heated in vacuum up to 350°C. Then gaseous hydrogen was put into the working chamber up to 2,3 MPa with rate of 0,1–0,2 MPa/min. Samples were exposed for 30 min in conditions and then cooled in isobar conditions. At cooling rates 3–5°C/min in temperature range 230–250°C there was fixed on videofilm a local swelling of the samples surfaces. The swelling grew up in isothermal conditions, reached maximum size, then began regress and disappeared (Fig. 1).

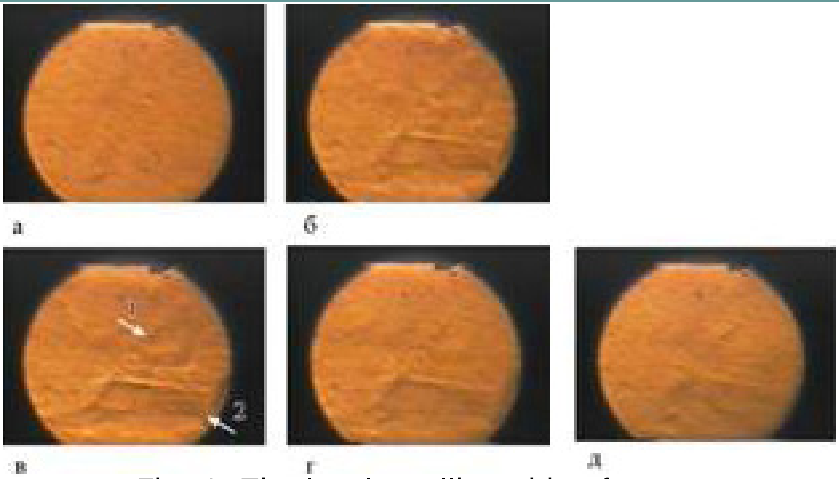

Fig. 1. The local swelling video frames

The reasons of the effect we explain by strong internal stresses influence. These stresses are generated in subsurface layers of the samples by hydrogen concentration gradients, and rearrangements of hydrogen solved before. Internal stresses don't overhead hear the elastic limit and relaxes with hydrogen concentration gradients decreasing.

Grains shift. In these experiments palladium and PdH_x were extremely quickly saturated with hydrogen ("hydrogen impacts"). Intensive hydrogen saturation of pure palladium doesn't change preliminary polished sample surface. But samples containing even very small quantity of preliminary dissolved hydrogen $PdH_{0.019\text{ - }0.038}$ change the surface very much as well as it shown at Fig. 2.

The reasons of the effect are hydrogen concentration stresses, generating in the sample during quick saturation with hydrogen.

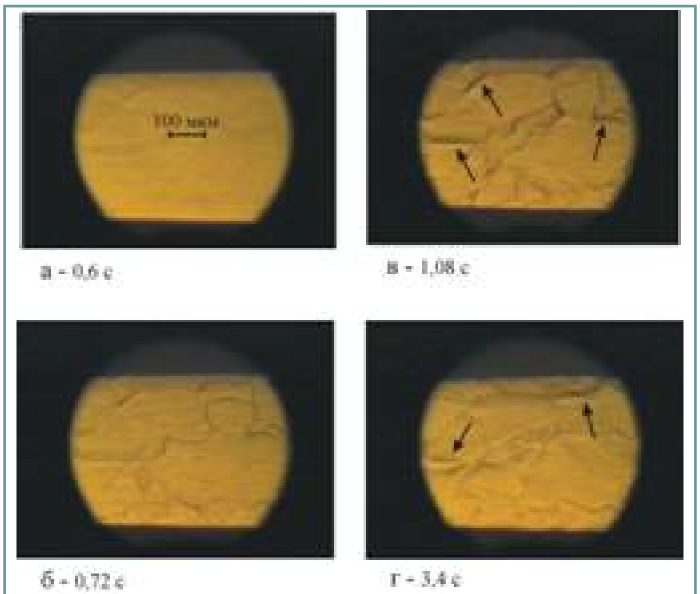

Fig. 2. Video frames of grains shifts
on the $PdH_{0.027}$ alloy surface at
hydrogen impact (hydrogen rate 1,0 MPa/c)

Soliton on palladium surface. At 230°C in $PdH_{0,1}$ alloy subsurface layers there were fixed firstly grains shift then wave-like coherent movements, similar to solitons. A part of video-film demonstrating birth, life and death of soliton-like moving swelling is represented on http://donntu.edu.ua/hydrogen-community/soliton.zip.

We believe that appearance of these wave processes is a special mechanism of internal stresses relaxation in metal–hydrogen alloys, unknown before.