Defect structure evolution in the process of relaxation of the Pd-Y-H system

O V Akimova¹, A A Veligzhanin², R D Svetogorov², S V Gorbunov³, N R Roshan³ and G S Burkhanov³
¹Physics department, Lomonosov Moscow State University, Moscow 119991, Russia
²National Research Center Kurchatov Institute, Moscow 123181, Russia
³Baikov Institute of Metallurgy and Materials Science, Moscow 119334, Russia

E-mail: akimova@physics.msu.ru

Abstract. X-ray diffraction and high-precision scanning electron microscopy methods were used to study the long-term evolution of the defect structure of diffusion filter-membranes Pd-Y. Analysis of X-ray diffraction data and microelectronic photographs showed that the recovery of the dislocation structure in the membranes was not uniform. Differences in the processes of hydrogen conservation in the structure of membranes are determined reversible hydrogen doping. Preservation by alloy of superstructural ordered regions was detected.

1. Introduction

The influence of hydrogen on metal alloys is an active research area thrive, most attention is paid to determination of the structure of diffusion filter-membranes operating in aggressive hydrogen-containing media [1-3]. There are several technologies for cleaning hydrogen-containing media from impurities in selective diffusion of hydrogen, but only dense metal membranes based on palladium, whose permeability to other gases is infinitesimally small, provide the opportunity to obtain hydrogen of high degree of purification [1, 2]. In this context, the stability of the structure of metal dense diffusion membranes during hydrogen separation is very important, especially in view of the need to add other elements to palladium, for instance: Y, Ag, Pb, In, to improve the strength characteristics of diffusion filters.

One of the directions to solve this problem is to identify the effects that occur during hydrogenation. This facilitates finding minimally destructive regime that would least affect the crystal structure of alloys. Another direction is to determine the possibility of predictable changes in the properties of materials under reversible hydrogen exposure. The issue of interaction of hydrogen and dislocations is related to microscopic plastic deformation of polycrystalline metal systems and hydrogen induced deformation in them.

The aim of this work is to identify the effect of various types of hydrogenation on the surface stability of hydrogenated alloys and the relaxation of their structure. In this work, diffusion filter membranes of the long-relaxation states of the alloy Pd₉₃Y₇ are studied under various conditions of hydrogen exposure. Experimental data of the effect of hydrogen on the defect structure of filters and their surfaces are considered.
2. Samples and experiment

Membranes of composition Pd0.9Y0.1 possess high hydrogen permeability and hardness during maintenance in hydrogen containing gas mixtures when used as diffusion filters [1-3]. Films of alloy 50 μm thickness were prepared from high purity materials (≥ 99.9%) by electric arc melting and cold rolling of blanks on a four-roll rolling mill with intermediate vacuum annealing at a temperature of 900 ºC for 1 hour [1]. The specific hydrogen permeability of the alloy at 500ºC is 5.2 m³·mm/(m²·h·MPa0.5) [1]. Membranes (denoted as 1 and 2) have passed homogenizing annealing at 900ºC for 1.5 h after rolling and have a hardness of 200 kg/mm².

The X-ray diffraction (XRD) with synchrotron radiation source was carried out in the Debye transmission geometry using equipment at the XSA beamline of the Kurchatov synchrotron radiation (SR) facility [4]. The SR beam was made monochromatic using a silicon channel-cut monochromator with energy resolution of ΔE/E~10⁻⁴ and the main reflection from planes of type {111}. The diffraction patterns of the samples were obtained at the wavelength 0.8 Å. The samples were oriented perpendicularly to the beam. The scattering radiation was recorded by a two-coordinate detector Rayonix SX165. Two-dimensional XRD patterns (figure 1) were integrated into I(2θ) curves (figure 2) by “Dionis” software [5].

Analysis of diffraction profiles was carried out using the software package “Fityk” [6]. The approximation of interference reflections by several peaks was interpreted as a heterogeneous phase composition of coherent scattering regions (CSR) with indexes hkl.

XRD data were analyzed in accordance with the kinematic theory of diffraction [7]. The influence of homogenizing annealing on the structure of the alloy Pd0.9Y0.1 demonstrated in [8]. The superstructure reflections were observed in diffraction patterns for the alloy in the original (before hydrogenation) state. The experimental intensities of diffraction peaks were normalized to the theoretically calculated intensities [7]. The values of the normalized intensities from CSRs with different orientation enable us to estimate the texture in the studied alloy. For the original membrane [8], the ratio higher diffraction orders of reflections from the CSR(111) and CSR(100) is 1.4 (Table 1), which indicates a weak texture. The ratio of the normalized intensities corresponding to two orders of reflection from CSRs with identical orientation (Table 1) can be used to reveal the dominant influence of either first-class defects (vacancies, micro pores, dislocation loops of small radii and new phase nuclei [9]) or extinction [7].

Membrane 1 was subjected to hydrogenation at 450 ºC and a pressure of 1 atm using a Setaram thermogravimeter. Membrane 2 was subjected to hydrogenation at 300 ºC at a pressure of 16 atm in a Siverts type equipment. The hydrogen absorption of the membranes regions of (α→β) transformations have formed [10]. The α phase is the low concentration of hydrogen and β phase is high hydrogen concentration [2].

3. Experimental results and discussion

Figure 1 shows two-dimensional XRD patterns for original state of membranes and after hydrogenation and relaxation.

The locations of intense diffraction maxima correspond to the main phase of membranes and determine a face-centered cubic unit cell of the crystal lattice for membranes both before and after hydrogenation and relaxation. After collective action of hydrogen atoms on the crystal lattice, changes in the distribution of the intensity of reflections are observed in figure 1 (b-c). Comparing diffraction patterns in figure 1(a) and figure 1(b) (for original membrane and membrane 1) one observes that the higher diffraction order reflections are split into two lines (for membrane 1). This result is explained by the presence in membrane 1 of phase β and α, which have different hydrogen concentration and different the unit cell parameters (a) (Table 2). The resolution of diffraction patterns is lower at small angles XRD, so the nearest order diffraction reflections with indexes 111 and 200 are not split.

Profiles of the main structural reflections in the graph of I(2θ) (figure 2) indicate that both membranes are in the two-phase region (β+α) of the phase transformation. In figure 2 (a) one observes
distinct diffraction peaks for β and α phases for membrane 1, whereas for membrane 2 the α phase is manifested by wider and shorter peaks for larger diffraction angles (figure 2(b)).

![Figure 1.](image1)

Figure 1. Two-dimensional XRD patterns for alloy Pd$_7$Y: (a)-before hydrogenation (original state); after hydrogenation: (b)-12264 hours of relaxation membrane 1; (c)-11000 hours of relaxation membrane 2.

Diffraction patterns for membrane 2 indicate a greater degree of coherence of the boundary between β and α phases than in the crystal lattice of the membrane 1. The parameters of the elementary phase cells (Table 2) indicates that the β and α phase of membrane 2 lose hydrogen faster than the phase of membrane 1 this is. Regions of the β phase for membrane 1 contain at least 8% more hydrogen (ignoring the influence of vacancies), than regions of the β phase for membrane 2.

![Figure 2.](image2)

Figure 2. XRD patterns: (a)-for membrane 1; (b)-for membrane 2.

The inserts in figure 2 show details of the diffraction spectra at small angles and the reflections from the CSR(311) and CSR(111). One can see a superstructural maximum of the phase Pd$_7$Y defined in the original state of the alloy [8].

| Membrane | I$_{111}$/I$_{222}$ | β phase | α phase | I$_{111}$/I$_{222}$ | β phase | α phase | Original state |
|----------|---------------------|---------|---------|---------------------|---------|---------|----------------|
| Membrane 1 | 3.2                 | 3.3     | 1.8     | 3.4                 | 4.2     | 1.0     | 3.7            |
| Membrane 2 | 3.3                 | 3.8     | 4.2     | 2.4                 | 10.3    | 0.9     | 3.6            |
| Original state | 3.3                 | 3.8     | 1.8     | 1.0                 | 3.7     | 0.9     | 1.4            |
Under similar relaxation conditions (external temperature and atmospheric pressure) of membranes after hydrogenation, the development of subsystems of defects in hydrogenated structures differs significantly. This fact is confirmed by the form of the structural diffraction maxima, the ratios of normalized intensities (Table 1) as well as by the difference in the parameters of the elementary phase cells (Table 2) and the value of effective dimensions of CSR (hkl) (figure 3(b)).

Less intense structural reflections for membrane 2 (figure 2) may indicate differences in the rotation angle of crystallites than membrane 1. For membrane 1, the ratios of the normalized intensities of diffraction maxima in the β and α phases are slightly different and are close to similar values in the original state of the alloy (Table 1). The result obtained indicates a weakening of the texture of the membrane due to the influence of hydrogen and a similar effect of first-class defects [10] in its β and α phases. For membrane 2, a more complex picture of changes was found: a significant increase in the role of defects of the first class in CSR(111) with a weakening of their influence in CSR(100) compared with the initial state of the alloy. A rotation of the β phase crystallites in the crystallographic direction [111] was also found, which led to an increase in texture compared to the initial state of the alloy with a small rotation of α phase crystallites in the [100] crystallographic direction (Table 1).

Table 2. The unit cell parameter (a) of the phases of membranes.

| № membrane | \(a_\beta, \text{Å}\) | \(|a_{\beta m1} - a_{\beta m2}|, \text{Å}\) | \(a_\alpha, \text{Å}\) | \(|a_{\alpha m1} - a_{\alpha m2}|, \text{Å}\) | The difference phases cells parameters, Å |
|------------|----------------|-----------------|----------------|----------------|----------------------------------------|
| 1          | 3.9520±        | 0.0095          | 3.9126±        | 0.0002          | 0.0394                                  |
| 2          | 3.9425±        | 0.0001          | 3.9049±        | 0.0012          | 0.0376                                  |

The reader should note a good linear fit of the physical broadening of the diffraction reflections of the β and α phases of the membrane 2 by the function \(\tan \theta\) (figure 3(a)). For membrane 1, no such a fit was found probably due to greater influence by defects of the first class (Table 1).

Figure 3. (a)-diffraction broadening of reflections for membrane 2 by the function tan\(\theta\); (b)-effective sizes D of crystallites of the β and α phases of membranes by the hkl (m1-membrane 1, m2-membrane 2). The symbols \(\beta(\varepsilon)\) and \(\alpha(\varepsilon)\) in figure 3(b) denote the values of the effective size of the β phase crystallites of membrane 1 and the α phase of membrane 2. These values are determined by taking into account the influence of micro strains in crystallites and coincide with the crystallites sizes calculated using the Scherer formula [7].
For reflections from the CSR(100) of the β phase (figure 3(a)), a greater broadening is observed compared to reflections from CSR(111), which is determined by the accumulation of micro strains in the elastic-soft crystallographic direction [100] for palladium-based alloys [7]. In the α phase with a linear dependence of the physical broadening of the diffraction maxima for CSR(111) by the tanθ, their greater broadening is observed in comparison with diffraction reflections for CSR(100). This result is possible in the case of the prevailing effect of the dispersion of crystallites on the broadening of diffraction reflections, which is also observed in the case of membrane 1.

The crystallites of the β phase of membrane 1 are almost equiaxial (figure 3 (b)) and exceed crystallites of the α phase of "its membrane" by 3-4 times.

The β phase crystallites of membrane 2 are almost the same size as the α phase crystallites of its own membrane and are 2 times smaller than the β phase crystallites of membrane 1. These facts imply that there is a small influence of micro strains in the nanocrystalline hydrogenated structure membrane 2 and that after hydrogenation the recovery of the dislocation structure in the membranes was not uniform.

The differences found in the defect structure of the membranes by X-ray diffraction are confirmed by electron microscopic images of the surface of membranes in figure 4. One can see the deformations of surfaces hydrogenated membranes. For the surface of the membrane 1, the diffraction contrast makes the phase boundaries well defined, while for membrane 2, they are nearly indistinguishable (shown with arrows).

![Figure 4](image)

**Figure 4.** Electron microscopic images of the surfaces hydrogenated membranes after the relaxation: (a)-during 12264 hours -membrane 1; (b)-during 11000 hours -membrane 2.

4. Conclusion
The paper reports finding differences in the structural state of initially identical crystal lattices of diffusion filter-membranes of metal alloy Pd93Y7 under different conditions of hydrogenation and subsequent relaxation at room temperature and atmospheric pressure.

X-ray studies revealed different stages of retention of hydrogen by the alloy in the region of polymorphic phase transformation (β→α) and the preservation of superstructural ordering regions by the alloy in the processes of hydrogenation and subsequent relaxation during 12000 hours.

The analysis of the ratio of normalized intensities of diffraction reflections showed differences in the changes of the defect structure of membranes as a result of hydrogen influence.

The results obtained are important for determine action of the response of a promising membrane alloy to hydrogen exposure and for predicting reliable and safe operation of membranes in deep hydrogen purification processes.
Acknowledgment
We thank Dr. T I Lakoba for editing the English version of the manuscript.

References
[1] Burkhanov G S, Gorina N B, Kolchugina N B and Roshan N R 2011 Platinum Metals Rev. 55 (1) 3
[2] Al-Mufachi N A, Rees N V and Steinberger-Wilkens R 2015 Renewable and Sustainable Energy Reviews 47 540
[3] Conde J J, Maroño M and Sánchez-Hervás J M 2017 Separation & Purification Reviews 46 152
[4] Svetogorov R D, Dorovatovskii P V and Lazarenko V A 2020 Crystal Research and Technologies 55 (5) 1900184
[5] Svetogorov R D “Dionis”,“Diffraction Open Integration Software” Certificate of state registration of PC software No. 2018660965
[6] Wojdyr M 2010 J. Appl. Cryst. 43 1126
[7] Iveronova V I and Revkevich G P 1978 Theory of X-ray Scattering (Moscow: Moscow State University Press) p. 278
[8] Akimova O V, Veligzhnin A A 2019 Physics of Metals and Metallography 120 (10) 962
[9] Krivoglaz M A 1983 X-ray and Neutron Diffraction in Nonideal Crystals (Kiev: Naukova Dumka) p. 338
[10] Akimova O V, Veligzhnin A A, Svetogorov R D, Gorbunov S V, Roshan N R and Burkhanov G S 2020 Physics of Metals and Metallography 121 (2) 157