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Kinetics and morphology of the reverse β→α hydride transformation in thermodynamically open Pd–H system

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Abstract

The kinetics of degassing and reverse β→α hydride transformation initiated in the unstrengthened β-hydride of Pd in the thermodynamically open Pd–H system is studied. An isothermal kinetic diagram was constructed and its shape was similar to those of transformations in steel during heating. With optical microscopy in situ and video-registration methods the morphology of new α-phase precipitations is studied. It is shown that the process of α-phase generation in subsurface layers depends on the orientation of the grain crystal lattice to the surface. α-Phase nuclei grow in borders of the grain in which they were generated. It is shown that hydrogen macro-stresses may be generated throughout the whole volume of the β-hydride sample and they relax by means of grain borders appearance (mutual grains displacement). During the process of β→α transformation local internal hydrogen stresses may slow down both degassing and β→α transformation. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Hydrogen; Reverse hydride transformation; Optical microscopy in situ; Isothermal kinetic diagram

1. Introduction

The investigation of hydride phase transformations attracts a great amount of theoretical and practical attention. This is because many kinds of hydrogen treatment of materials are based on phase transformations induced by hydrogen [1,2].

It was shown in Ref. [3] that reverse β→α transformation develops by the mechanism of generation and growth. The kinetics of reverse β→α hydride transformation was investigated under isothermal conditions within 285–150°C [4,5]. It was shown [5] that the rate of β→α phase transformation slows with decreasing temperature much faster than could be expected as a result of simple diffusivity deceleration when the temperature decreases. It was suggested that the general factor influencing this slowing was the appearance of hydrogen stresses [5]. These hydrogen stresses are caused by hydrogen concentration gradients and by difference in β- and α-phases specific volumes.

In the present work the task undertaken was to continue both the study of kinetics of β→α hydride transformations in PdH_x alloys and to investigate the evolution of morphology of transforming phases.

2. Material and methods

Experiments were carried out in a new hydrogen-vacuum device HVD-2 specially constructed for this kind of experiment [6]. The HVD-2 affords a possibility to carry out experiments both in vacuum (~0.1 Pa) and in hydrogen (up to 2.5 MPa). The control of absorption, desorption and reverse β→α transformation development were fulfilled by measuring the sample electrical resistance. At the same time preliminary polished surface of the sample may be controlled with optical microscopy method in situ as to emergence of a surface relief caused by a hydride transformation. Using the HVD-2, video registration of hydride transformation process is possible and then video-data can be examined with a Pentium video card frame by frame. This method of video type recording for data examination by computer can register a very quick process when simple photographing is inert.

Pure palladium was studied in this work (admixtures are the following (weight%): Pt, 0.009; Rh, 0.002; Fe, 0.009). Wire samples with a diameter 0.5 mm×23 mm long were preannealed in vacuum at 1000°C for 1 h. Then the sample under investigation was put into the working chamber of the HVD-2, and heated in vacuum up to 350°C. Then, the chamber was filled with hydrogen (0.1 MPa/min) up to 2.3 MPa. These conditions ($T=350$°C, $P=2.3$ MPa) are higher

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than the critical point of the Pd–H system conditions, i.e. 292°C and 1.97 MPa [7]. So, a palladium sample was saturated with hydrogen at a rather slow rate in the homogeneous solid solution field of the Pd–H equilibrium diagram.

Hydrogen absorption by Pd was controlled by measuring sample electrical resistance. After the electrical resistance increase ended, the sample was additionally maintained at 350°C, 2.3 MPa for 10 min. Then the sample was cooled (1–2 K/min) and a representative point of the Pd–H system was moving along the isobar of 2.3 MPa. After reaching an experimental temperature between 100 and 200°C, the hydrogen pressure was decreased slowly to 0.1 MPa for 100–150°C and to 0.37 MPa for 200°C.

As a result, the whole palladium sample was transferred into the β-phase state of the composition according to the β-phase of palladium on the equilibrium Pd–H diagram. This fully β-phase palladium has a low defect structure, and palladium saturated with hydrogen in such a way is an alloy of PdH_x composition and can be called β-hydride of palladium. The sample has not undergone hydrogen phase naklep (cold work) [8], was not strengthened, and saved its annealed structure.

An isothermal reverse hydride transformation and degassing of the sample were initiated by hydrogen pressure decrease in the working chamber of the HVD-2. Then, during an experiment the pressure in the working chamber was about 0.1–1.5 Pa.

Hydrogen pressures of 0.1 and 0.37 MPa are critical for temperatures 150 and 200°C, respectively. It means that β→α transformation starts developing immediately after the pressure decreases. For lower temperatures critical hydrogen pressure is less than 0.1 MPa. This is why β→α transformation was developed in these experiments: hydrogen contents were diminished in the sample, first till critical hydrogen content in the β-phase region; then, β→α transformation began.

3. Results and discussion

Characteristic curves of sample electrical resistance changing are shown in Fig. 1 for $T=100°C$ (Fig. 1A), 140°C (Fig. 1B) and 150°C (Fig. 1C). β, (α+β) and α-fields according to the equilibrium diagram of Pd–H system are marked. As shown in Fig. 1A, at 100°C degassing of a sample was developed just in β-field and there was no transition to the (α+β) domain. At 110 and 125°C (not shown in Fig. 1) the full degassing of a sample in β-field was completed and β→α transformation development started. But it was stopped when 23 and 80% of α-phase were reached at 110 and 125°C, respectively. This tendency is illustrated in Fig. 1B (140°C) where β→α transformation is braked when 83% of α-phase are reached. At 150°C (Fig. 1C) β→α transformation was developed and completed in 180 min. The sample degassing was slowing down in the α-field.

When the hydrogen pressure was decreased from $P_{H_2} =$ 3.7 MPa (at 200°C), β→α transformation was developed and its rate at the first stages was three times of that at 150°C. So, the β→α transformation was completed in 95 min.

Slowing down of palladium β-hydride degassing (100°C), β→α transformation (110–140°C) and sample degassing in the α-field (150°C) described are not connected with surface processes as the sample surface was well activated by means of multiple saturations and degassings of hydrogen in a wide range of temperatures (see Section 2).

As discussed in detail in Ref. [5], a described slowing down of degassing and β→α hydride transformation is caused by hydrogen elastic stresses occurrence, which are connected with hydrogen concentration gradients appearance and with the difference of β- and α-phases specific volumes. As the difference between α- and β-phases specific volumes diminishes, and diffusivity of hydrogen accelerates then the slowing down gradually becomes weaker. It leads to full completion of β→α transformation at temperatures higher than 150°C.

Let us assume that the time of degassing completion depends on diffusivity only. Then, calculations based on known coefficients of diffusion and Fick's laws, showed that time of sample degassing must be 3 min for 150°C and 1 min for 200°C. Experimental time of degassing (Fig. 1) is 60–100 times longer than calculated values.

Then, kinetic curves of β→α transformation (% of a formed α-phase as function of time) were constructed following the kinetic curves (ρ–τ), corresponding to (α+β) field and electrical resistance of pure palladium at respective temperatures. By constructed kinetic curves the isothermal diagram of reverse hydride β→α transformation in a thermodynamically open Pd–H system was drawn (Fig. 2). This diagram has quite another type of shape to that of a direct α→ β transformation. Indeed, isothermal diagrams of a direct α→β hydride transformation initiated by cooling (or by hydrogen pressure increasing) [9] are C-shaped. This is evidence of a quick acceleration of a new β-phase nuclei generation rate in case of a direct α→β transformation, when temperature decreases (overcooling rate is increased). That is why the rate of α→β phase transition also grows at first (though diffusivity of hydrogen decelerates with temperature decrease). Then, hydrogen diffusivity begins to prevail, and due to this fact the rate of α→β direct transformation starts to slow down passing through the maximum of its value.

The isothermal diagram in Fig. 2 shows that in case of a reverse β→α hydride transformation temperature increase causes acceleration of the transformation rate only, which is similar to transformations in steels during heating [10]. This is evidence that the temperature rise causes both hydrogen diffusivity acceleration and rate of a new α-

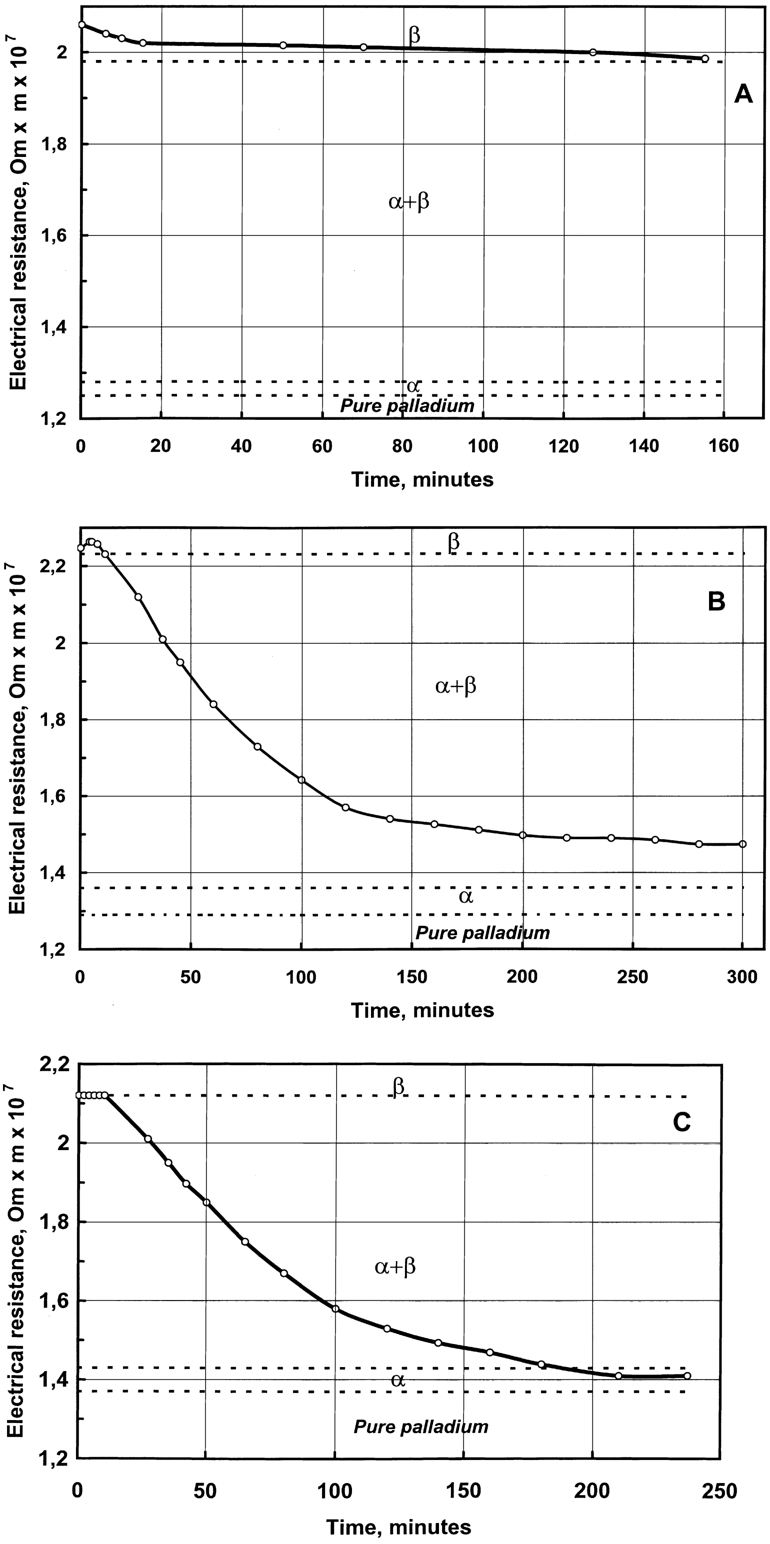

Fig. 1. Electrical resistance changes depending on time at different temperatures (A) 100°C; (B) 140°C; (C) 150°C.

phase nuclei generation. Obviously, this principle is the main difference of a reverse β→α and direct α→β hydride transformations in a thermodynamically open Pd–H system.

The morphological peculiarities of a reverse β→α hydride transformation were then studied. An in situ video-registration of a sample polished surface state and the changes occurring in it were carried out in real time (magnification of the optical microscope MT-7 is 70 times). During the process of hydrogen saturation of the

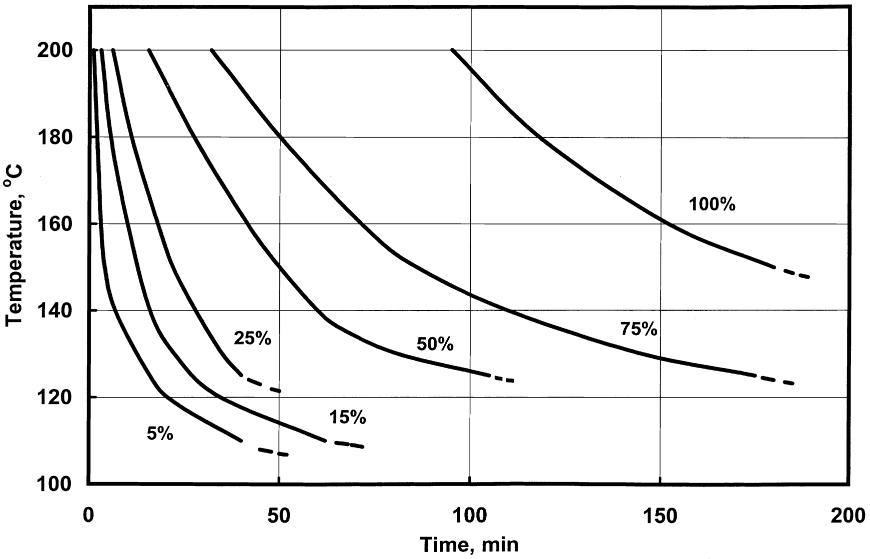

Fig. 2. Isothermal diagram of reverse hydride β→α transformation.

sample according to the method described above, the polished surface did not undergo change (Fig. 3a). However, grains of the sample were micro-displaced, respectively to each other when the temperature decreased from 350°C to room temperature at constant pressure of 2.3 MPa (in β-field) and then the hydrogen pressure was decreasing from 2.3 MPa to 0.1–1.5 Pa. As a result, grain borders became visible at the polished surface of the sample (Fig. 3b). This fact demonstrated occurrence of the hydrogen macro stresses described above which were caused by hydrogen concentration gradients appearance in the process of β-phase degassing. Grains shifting with respect to each other (Fig. 3b) is a result of partial relaxation of stresses mentioned above. An important fact is that the surface of each separate grain remains plane and undeformed. This proves that stresses causing grain displacement are macroscopic ones and they act throughout the whole sample.

Then, temperature increased and when 125°C was reached, first precipitates of α-phase were fixed. Fig. 3c demonstrates six α-phase nuclei. One of them has grown rather (marked with pointer 1), others are on the first stage of development (pointer 2).

The generation of new and growth of marked α-phase precipitates are well visible in Fig. 3d and e. Generally they have a massive form. Fig. 3f shows the final stage of β→α transformation in subsurface layers of a sample.

Video-registration analysis helped to reveal the following morphological peculiarities of a reverse β→α hydride transformation. In accordance with Ref. [3], that transformation was carried out by classic mechanism of generation and growth. Generation of α-phase in subsurface layers depends on the grain crystal lattice orientation as to the grain surface. It is possible to see in Fig. 3c where all visible nuclei are formed just in one grain, and nuclei start appearing in other ones (Fig. 3d and e). Precipitates of hydride α-phase, being generated in one grain, are gradually growing and filling all its grain without transition to a neighbour one. Other grains undergo transformations by their own nuclei of α-phase.

It is important that generation and development of each nucleus are accompanied by local elastic hydrogen stresses appearance because of specific α- and β-phases volumes difference and presence of local hydrogen diffusivity gradients. When the stresses excel yield-point, the local plastic deformation of both growing α-phase nuclei and surrounding β-phase happens. As a result, unreversible plastic changes of a sample surface occur and they also take place after degassing of the sample.

So, video-type-recording of sample surface changes during the process of hydrogen saturation, following degassing and β→α transformation let us study morphological peculiarities of β→α hydride transformation. It gives an experimental confirmation of the appearance and relaxation of macroscopic internal stresses throughout the whole sample during the process of palladium β-hydride degassing. At first stages of β→α hydride transformation local internal stresses occurred and relaxed nearby α-phase nuclei.

At the final stages of the transformation separate α-phase nuclei begin integrating and the sample as a whole goes into its complex-stressed state. Results of a particular relaxation of that complex-stressed state can be seen in Fig. 3f.

4. Conclusion

Kinetics of degassing and reverse hydride β→α transformation in a thermodynamically open Pd–H system are

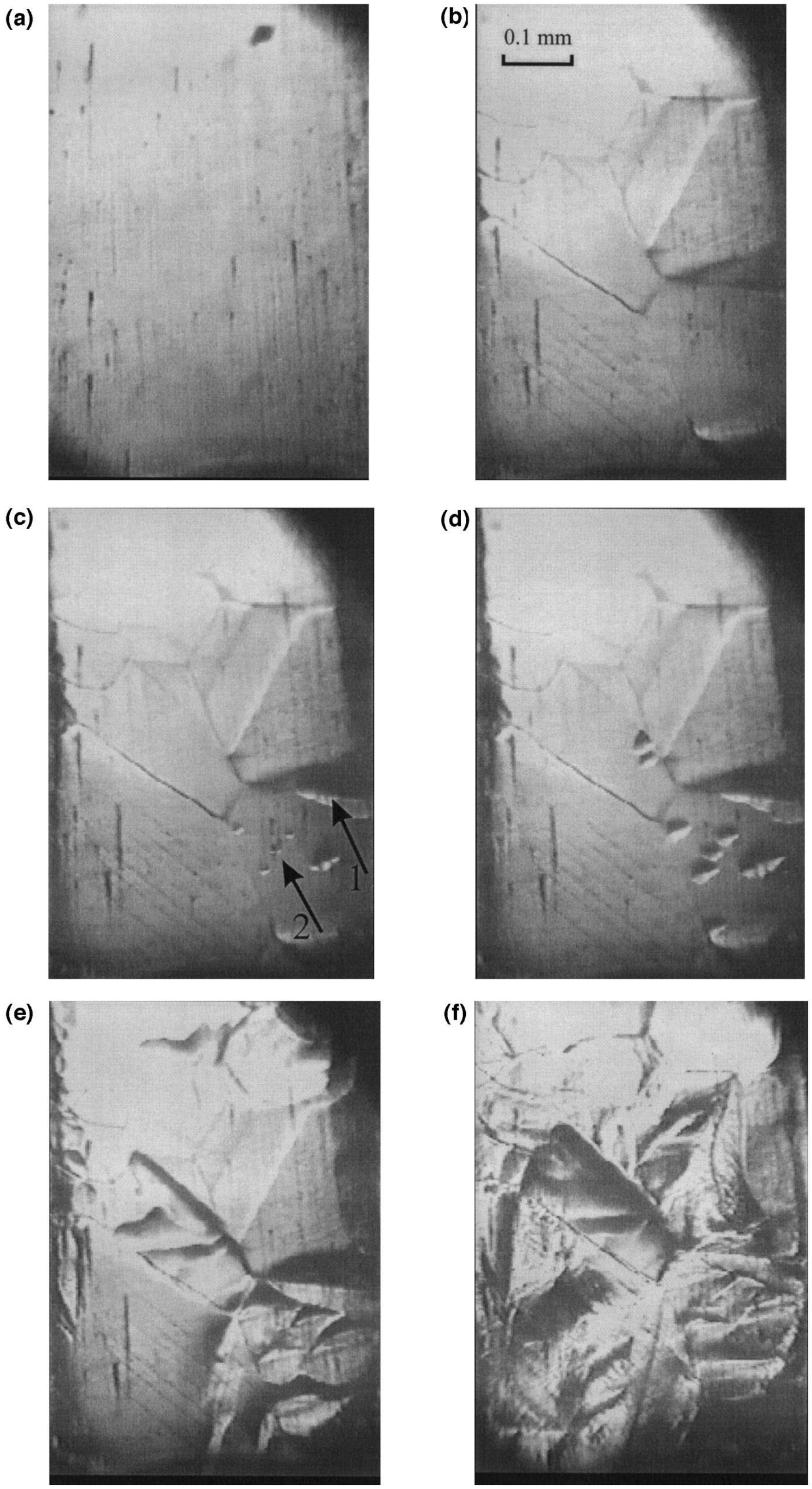

Fig. 3. Morphological peculiarities of reverse hydride β→α transformation: (a) preliminary polished surface of the sample when saturating with hydrogen (b) appeared grain borders after cooling and depression, 0 s (c) 4 s after transformation start (d) 5 s (e) 18 s (f) 5 min 20 s.

investigated. It is shown, that within 100–200°C the isothermal diagram of β→α transformation differs greatly from that of α→β transformation and is analogous to that of transformations in steel during heating. As follows from the type of the isothermal diagram of β→α hydride transformation, when parameters (T, P_{H_2}) are changed, the rate of α-phase nuclei generation and their growth change in the same direction, namely in the direction of transformation rate increasing.

There is also in situ confirmation, that β→α transformation is carried out by the classic mechanism of generation and growth in mentioned experimental conditions. α-Phase generation in subsurface layers depends on the grain crystal lattice orientation as to the surface. α-Phase precipitates usually grow in borders of their own grain.

Degassing of the sample which is in the β-hydride condition results in the appearance of macroscopic internal stresses in the whole sample volume. Displacement of grains along their borders is one of the mechanisms of these stresses relaxations. Generation of α-phase and its growth results in local plastic deformation.

Internal hydrogen stresses evoke braking of degassing and β→α transformation in a thermodynamically open Pd–H system.

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