

Discovery of spontaneous deformation of Pd metal during hydrogen absorption/desorption cycles

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(Contributed by Toshimitsu YAMAZAKI, M.J.A.)

Abstract: A drastic deformation was observed in Pd metal of various shapes after hydrogen absorption and desorption cycles at 150 °C at a gas pressure of 1–5 MPa. All of the phenomena observed indicate that some strong internal force is induced spontaneously during hydrogen absorption/desorption cycles to produce a collective deformation so as to minimize the surface.

Keywords: Pd metal, hydrogen in Pd, spontaneous deformation, hydrogen absorption, hydrogen desorption

1. Introduction

The subject of hydrogen in metals, particularly in Pd, which absorbs a large amount of hydrogen, is currently of great importance from the viewpoint of hydrogen storage and embrittlement.¹⁾ From the known phase diagram in the pressure (P) and temperature (T) domain, the application of H₂ gas at $P = 1$ MPa to Pd metal at $T = 150$ °C quickly saturates H in Pd to about a 70% atomic concentration (it takes about 10 min for 1 mm-thick Pd metal). When the outer gas is evacuated, the absorbed hydrogen goes away. After this cycle, the Pd metal is believed to return to the original state. In the present paper we report an unexpected observation of a drastic change in the shape of Pd metal after hydrogen absorption/desorption cycles. This paper reports on the first results of our observations. Some systematic experiments were also made, including X-ray structure analysis.

2. First encounter with a peculiar deformation

This phenomenon was discovered rather accidentally, while we were investigating exotic phenomena of dense deuterium in nanoscale Pd metal powders, as reported by Arata and Zhang.²⁾ We used a double-structure Pd-SUS vessel, which was invented

by Professor Y. Arata, and which was kindly provided to us. It was composed of outer and inner vessels, as shown in Fig. 1 (left). The inner vessel was a Pd cylinder of 12-mm outer diameter, 10-mm inner diameter and 60-mm length, both ends of which were brazed to SUS components. The outer vessel was a SUS container, which housed the inner vessel. Both the inner and outer vessels could independently be evacuated or filled with high-pressure hydrogen gas. Following the procedure of an experiment of Arata and Zhang²⁾ we kept the whole vessel at 150 °C under a high vacuum ($\sim 10^{-4}$ Pa), and filled D₂ gas of $P = 5$ MPa to the outer vessel. The deuterium gas penetrated through the Pd cylinder into the inner space, where nanoscale-Pd in the form of (Pd)₃₅-(ZrO₂)₆₅ powders³⁾ was located. After some time, the deuterium gas was evacuated to search for any exotic residue produced in the inner cylinder. We repeated this type of experiment several times, and when we opened the whole vessel, we found that the inner vessel had been tremendously deformed.

We show in Fig. 1 (right) the deformed inner vessel in comparison with the unused one. The Pd cylinder part was drastically shrunk both in the length (from 60 mm to 52 mm) and diameter (from 12 mm to 10 mm). At first glance, the Pd pipe seemed to have been crushed by the outer gas pressure; a transient D₂ gas pressure in the outer vessel may have been a cause. To test this hypothesis we evacuated the outer space, and charged D₂ gas of 5 MPa into the inner cylinder. Still, we observed the same “crushed” shape, even with an inner pressure of 5 MPa. This meant that the deformation was

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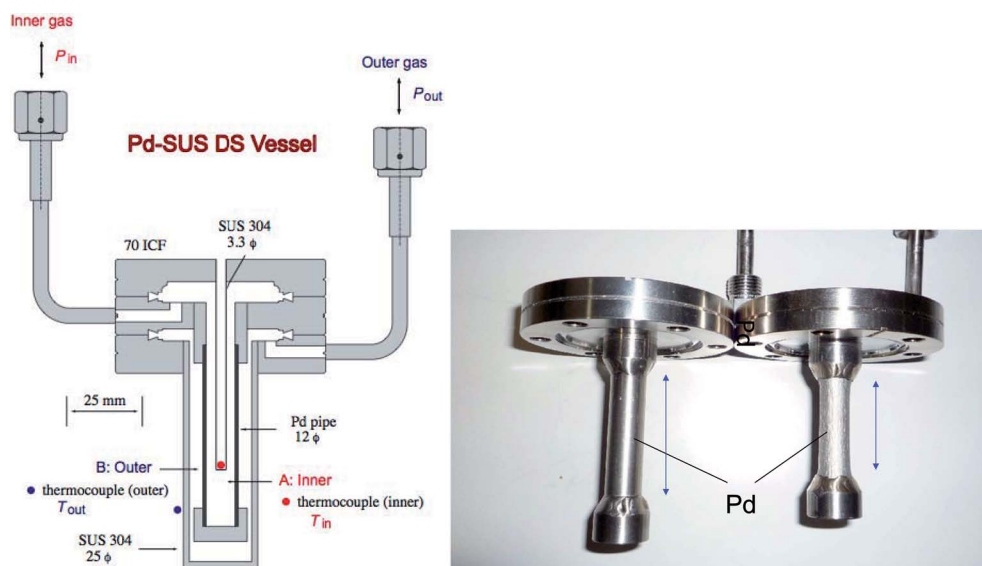


Fig. 1. (Left) Layout of the double-structure vessel invented and provided by Arata.²⁾ (Right) Photograph of the inner Pd cylinder, before (left) and after (right) the hydrogen absorption/desorption cycles (about 10 cycles).

caused, not by gas pressure, but by some internal force. At this stage, the deformation was recognized between the treated and untreated vessels both at room temperature, and it was not known at which instance the deformation took place during the incubation cycle. We thus attempted to measure the displacement *in situ* at a temperature of 150 °C at which hydrogen was absorbed and desorbed.

3. *In-situ* measurements of the deformation

For this purpose we set up a laser reflection device to measure the displacement of the Pd cylinder in the length direction (at the position of the SUS edge), which was enclosed in another SUS vessel with a sapphire window for a laser beam. This device is capable of measuring a displacement to μm precision. We kept the whole system at 150 °C to avoid any trivial thermal expansion effect, and charged D_2 gas of 5 MPa. As shown in Fig. 2, the displacement increased toward expansion and reached a saturation value of about 0.5 mm. This is understood as being an expansion effect caused by hydrogen absorption. We then purged the hydrogen gas and evacuated the vessel. A quick displacement in the opposite direction was observed, followed by a slow movement of the position, reflecting a hydrogen desorption effect. Surprisingly, the position was found to exceed the original position and to end up with a 0.5 mm contraction compared with the original position. Suc-

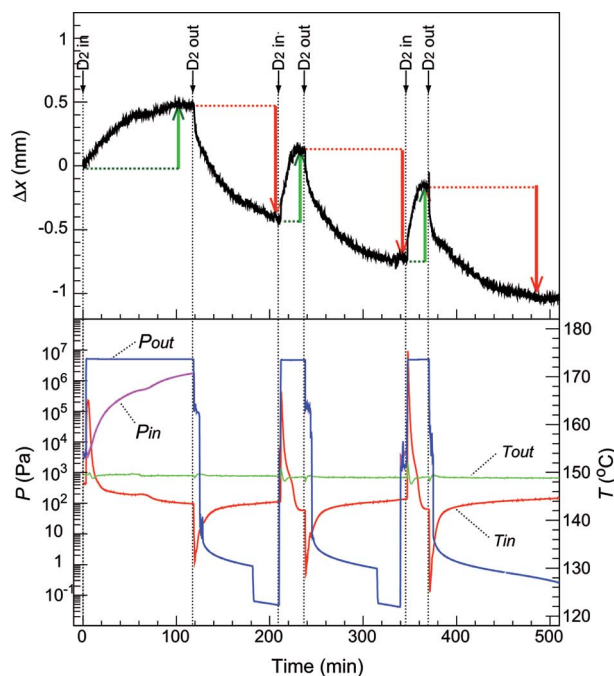


Fig. 2. Displacement of the inner Pd cylinder vessel in the length direction with the elapsed time during repeated hydrogen absorption and desorption cycles. The timings of hydrogen-in and -out are shown. The green and red arrows indicate expansion and shrinkage at the hydrogen absorption and desorption, respectively.

cessive runs demonstrated that an anomalous shrinkage of as much as 0.5 mm was always produced and accumulated after every cycle of hydrogen absorp-

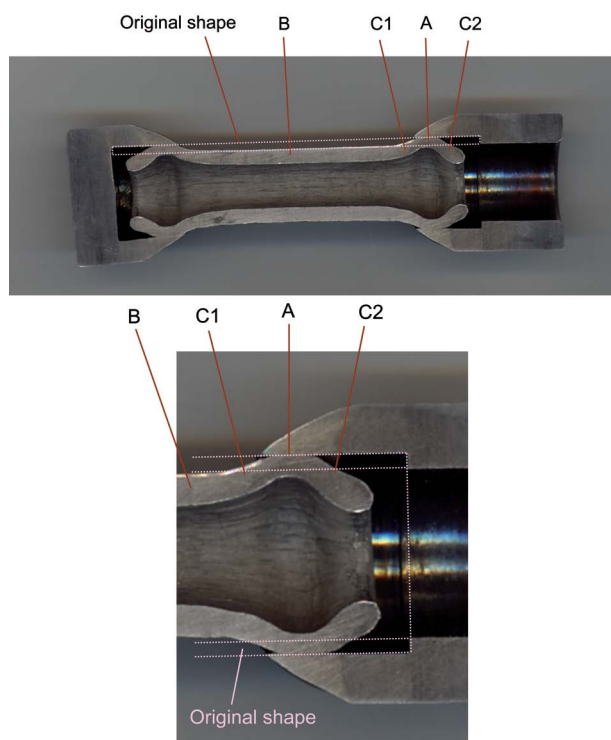


Fig. 3. Cross sectional view of the deformed Pd vessel. A: Pd cylinder joined to SUS part (diameter unchanged), B: Central part of the uniformly shrunk Pd cylinder, C1 and C2: highly deformed parts near A. The original shape of the Pd cylinder is outlined by dotted lines.

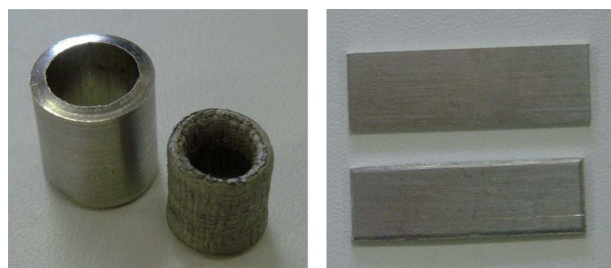


Fig. 4. Photographs of free Pd cylinders and plates before and after the hydrogen absorption/desorption cycles.

tion/desorption. The variation of the displacement went on slowly in correlation with the evacuation time of about 100 minutes.

To investigate what had really happened to this Pd cylinder we cut it in half. The cross section of the cut-off vessel, as shown in Fig. 3, revealed very interesting aspects. First, the edge part (A) of the Pd cylinder was found to have remained firmly joined to the SUS part. On the other hand, the central part of the Pd cylinder (B) was rather uniformly com-

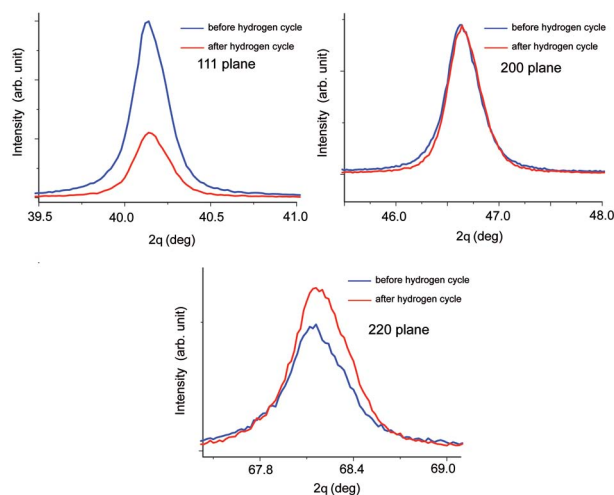


Fig. 5. X-ray diffraction patterns for two Pd plates, before (blue) and after (red) the hydrogen cycles.

pressed, and its end was connected to the joined edge in a very deformed shape ("C1"). The outer diameter was reduced from the original 12 mm to less than 10 mm, and its length was also decreased tremendously. The inner diameter was very much reduced so that the total amount of Pd was preserved. Surprisingly, both of the open ends of the Pd cylinder ("C2") were largely distorted spontaneously, nearly in the same shape as the C1 part. The highly distorted parts (C1 and C2) were peeled off from the joined SUS part. These observations indicate that the distortion occurs collectively, driven by some spontaneous strong force. The strength of the internal stress to cause this distortion can be estimated to be on the order of 600 MPa, which is the force needed to break the Au-Ni joint.⁴⁾ It can also be estimated from an observed slight deformation of the SUS lid.

4. Systematic studies

We were curious to see whether this peculiar distortion is specific to the present Pd cylinder joined to a SUS vessel, or is of more general character. We thus investigated this effect in other shapes of Pd metal. As shown in Fig. 4, a simple Pd cylinder (12-mm OD and 20-mm length) treated in 12 hydrogen cycles revealed the same effect. A Pd plate ($W = 10$ mm, $L = 30$ mm and $T = 1.00$ mm) treated as well became shrunk in the direction of the plate, while its thickness was slightly increased so that the total volume was conserved. Note that the compression of the

Table 1. Observed deformations of various Pd samples after 150 °C, 1 MPa H₂/D₂ cycles (units in mm)

Shape		Before	After	Shrinkage ratio	Number of cycles	Displacement per cycle
Cylinder	Length	20.00	17.50	0.875	12	−1.04 %
	Outer Dia	12.00	10.70	0.89	12	−0.92 %
	Inner Dia	10.00	8.0	0.80	12	−1.67 %
Plate	Length	29.9	28.7	0.960	3	−1.33 %
	Depth	9.3	9.15	0.983	3	−0.57 %
	Thickness	1.01	1.08	1.069	3	+2.3 %
Wire	Length	60.60	52.80	0.87	12	−1.08 %
	Dia	1.000	1.085	1.085	12	+0.71 %

Pd cylinder occurred both in the diameter and the length, while maintaining the volume (and the density). On the other hand, a plate or wire shrinks in length and, accordingly, the thickness was increased so as to keep the volume. The measured effects are presented in Table 1. We also tested a Pd plate (10 mm × 30 mm × 1 mm) well annealed at 1000 °C. The same sort of distortion with even an enhanced effect was observed.

From this observation we learned that the peculiar deformation is a general property of Pd metal: *the deformation always occurs so as to minimize the surface*. The sharp edges of the Pd cylinder and plate became round after the hydrogen cycle (Fig. 3 and 4). We found that this general deformation effect occurs for both hydrogen and deuterium, and also at 1 MPa at 150 °C.

5. Lattice constant

It is extremely interesting to study whether the Pd lattice constant changes or not after the hydrogen cycle. For this purpose, x-ray diffraction patterns were taken for the two samples before and after the hydrogen cycle. The results shown in Fig. 5 indicate that there is no drastic change in the lattice constant after such a violent deformation process.

6. Summary: spontaneous and collective super deformation

We summarize our observations as follows:

- 1) A large distortion on Pd metal is caused during hydrogen absorption and desorption cycles at 150 °C and 10 MPa. Every cycle produces a definite amount of deformation, which is accumulated in successive cycles. This general phenomena was observed even in an enhanced manner for a well annealed sample beforehand.

- 2) A large internal stress is what produces the deformation on a large scale. It has a characteristics of surface tension.
- 3) The lattice constant of Pd is nearly unchanged before and after the hydrogen cycles.

All of the phenomena we have observed indicate that some strong internal force is induced spontaneously during the hydrogen absorption/desorption cycle to produce a collective deformation so as to minimize the surface. Further experiments are in progress to understand the mechanism of this peculiar deformation.

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