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Hydrogen elasticity phenomenon: Experimental manifestations and theory

V.A. Goltsov, Zh.L. Glukhova*, O.A. Minakova

Donetsk National Technical University, Artema Str., 58, Donetsk 83000, Ukraine

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Abstract

Deformation of a palladium plate upon its one-side saturation with hydrogen and subsequent degassing in a temperature range of 150–100 °C has a regular manner. During the full cycle of hydrogen saturation–degassing it is almost completely reversible. At the saturation it is possible to arbitrarily distinguish a reversible and residual component of the deformation. As the temperature of saturation in lowered from 150 to 100 °C, the contribution from the reversible and residual components into the total deformation changed fundamentally. It was theoretically shown that one cause of the residual deformation of plate is the stabilization of the saturation process (without final equalization of the hydrogen concentration), which is due to the retardation of hydrogen diffusion by hydrogen-induced elastic stresses that arise upon deformation.

Keywords: Metals; Gas–solid reaction; Elasticity

1. Introduction

The hydrogen elasticity is a fundamental phenomenon, which experimental and theoretical study is of great importance both for developing the theoretical basis of hydrogen treatment [1–4] and solving problems of hydrogen-induced degradation and failure of materials [4]. The nature of the hydrogen elasticity (HE) phenomenon is as follows. Internal hydrogen atoms expand a solid crystal lattice. Hence, any inhomogeneities in hydrogen arrangement and any concentration gradients of hydrogen cause the appearance of a corresponding nonhomogeneous and nonsimultaneous expansion of a crystal lattice, and relative stresses that are called hydrogen concentrational (HC) stresses. Fields of HC-stresses in their turn influence hydrogen diffusion and cause a rearragement of hydrogen concentration fields and so on. So, it is evident that any changing of hydrogen concentration fields and HC-stresses fields are intercaused and interrelated by dynamic processes.

The hydrogen elasticity phenomenon takes place in metals, compounds and other materials in “pure state” when hydrogen stresses do not overcome a material limit of proportionality. Hydrogen elasticity phenomenon is subdivided into hydrogen elastic mechanical effects (a macroscopic reversible form-changing effect, Gorsky effect, a reversible coherent swelling of a surface), and hydrogen elasticity diffusive effects [5], e.g., slowing down of a hydrogen diffusive flow, an uphill hydrogen diffusive slow, Lewis effect, thermo-baro-elastic-diffusive equilibrium effect [4,6]. The task of this study was to investigate macroscopical manifestation of HE-phenomenon through the deformation of palladium plate upon its one-side saturation with hydrogen.

2. Experiments and results

As the material for the investigation, we used palladium that contained the following impurities (wt.%): 0.009% Pt, 0.002% Rh, 0.009% Fe, and 0.001% Si. Specimens in the form of plates with dimensions 68 mm × 5.5 mm × 0.28 mm were annealed at a temperature of 600 °C for 1 h in a vacuum

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* Corresponding author. Tel.: +380 62 305 02 35; fax: +380 62 304 12 78.
E-mail address: glukhov@ukrnimi.donetsk.ua (Zh.L. Glukhova).

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of 10^{-2} mmHg and cooled with a furnace to 20 °C. Then, one side of the specimen was electroplated with cooper (1.5 μm). Since the hydrogen permeability of copper is by several orders of magnitude less then that for palladium at the experimental temperatures, the copper film of this thickness, according to estimations, serves as an impermeable membrane for hydrogen. The specimen was horizontally fixed at one end in the working chamber of a vacuum-hydrogen apparatus with the copper-coated side facing upward. Correspondingly, the plate deflections observed through a special window upon hydrogen absorbtion were upward (positive). The displacement was measured by cathetometer to an accuracy of ±0.02 mm.

Diffusion-purified hydrogen was quickly (within 1–5 s) let into the working chamber to a specified pressure. The pressure has been varied from 3×10^3 Pa to a pressure, which corresponded to the critical value for the $\alpha \rightarrow \beta$ transformation at experimental temperature (for 150 °C – 1.1×10^5 Pa, for 140 °C – 0.8×10^5 Pa, etc.). The specimen was held at this pressure from 0.5 to 1 h until it came into a steady state. Then, the chamber was degassed and hydrogen was being evacuated from the specimen until it achieved a steady state (0.5–1 h). A typical curve of the sample deflection as a function of time of hydrogen saturation under the isobaric exposure is given in Fig. 1. A rapid increase of hydrogen pressure in the chamber always causes an intense increase in the specimen deflection from zero to its maximum (site A). As hydrogenising continues, the specimen is gradually saturated with hydrogen and hydrogen concentration levels off, which leads to a decrease in the concentration gradients and related internal stresses. The specimen straightens, i.e., deflection gradually decreases (site ABC). It is surprising that in all cases of a one-sided saturation of palladium plate considerable large change in the form of a plate took place.

When hydrogen is evacuated from the chamber and the specimen is degassed, a similar curve (but reverse) is observed (site DEF). However, the deformations for the full saturation–degassing cycle were almost completely reversible. The hydrogen-induced elastic deformation of the palladium plate was studied depending on the hydrogen pressure in the α solid-solution field in the range of 150–100 °C.

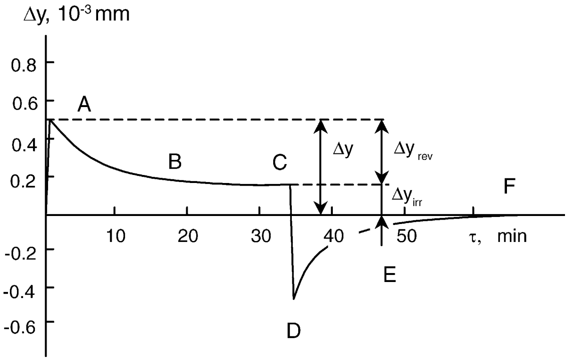

Fig. 1. Time dependence of the specimen deflection upon hydrogenation at an enhanced hydrogen pressure, isobaric holding, and subsequent degassing ($T = 150\,°\mathrm{C}$, $P = 7 \times 10^4$ Pa).

The main results are as follows. Upon one-side hydrogen saturation at different pressures and temperatures, the palladium plate changes its shape in a regular manner. During the complete saturation–degassing cycle, the deformation can be considered reversible. In the stage of the hydrogen saturation the deformation can arbitrarily be divided into two components: reversible and irreversible. As the temperature of saturation in lowered from 150 to 100 °C, the maximum deformation of the plate also decreases. The contributions of the reversible and residual components into the total deformation changes. At 150 °C with increase of hydrogen pressure the total form changing and its reversible component grow. Irreversible one practically does not change. On the contrary, at 100 °C, reversible component behaves conservatively. With increase of hydrogen pressure total form changing and irreversible component grow.

3. Discussion

Since we work in a single-phase region, there are no phase transformations. Arising elastic stresses do not exceed the yield stress. Therefore our work deals only with elastic stresses. The following hypothesis has been made. One of the reasons of the Δy_{irr} existence is that hydrogen elastic stresses slow down hydrogen diffusion so much that hydrogen concentration has not managed to level off along the plate width during an instrumental time. As a result, the residual HC-stresses and a plate residual deformation (Δy_{irr}) take place. When analyzing the above regularities of the deformation of the palladium plate during its one-side saturation with hydrogen, we used equations of the hydrogen elasticity phenomenon [6]. For the one-dimensional case, the system of equations of hydrogen elasticity takes the following form:

$$\frac{\partial^2 c}{\partial x^2} - \frac{1}{D}\frac{\partial c}{\partial t} - \frac{(3\lambda + 2\mu)}{D} w B_{\mathrm{c}} c \frac{\partial^2 u_x}{\partial x \partial t} = 0, \qquad (1)$$

$$(\lambda + 2\mu)\frac{\partial^2 u_x}{\partial x^2} - \frac{(3\lambda + 2\mu)}{D} w \frac{\partial c}{\partial x} = 0, \qquad (2)$$

where c is the atomic fraction of hydrogen, u_x the x component of the displacement vector, λ and μ are Lame's constants, w the coefficient of linear expansion of the metal due to the change of hydrogen concentration, D the hydrogen diffusion coefficient, $B_{\mathrm{c}} = \mathrm{d}c/\mathrm{d}P$ the hydrogen capacity determined from the experimental P–T–c diagram for the Pd–H system, and P is the hydrogen pressure in the gas phase. The diffusion coefficients were calculated for each temperature according to [7].

The system of Eqs. (1) and (2) was computed numerically by replacing the partial differential equations with corresponding finite-difference equations. The initial and boundary conditions for the system were as follows:

$$c(x,0)=0 \quad \text{for} -\frac{h}{2}\le x\le\frac{h}{2},$$
$$c(x,0)=c_0 \quad \text{for} -\infty<x<-\frac{h}{2} \quad \text{and} \quad \frac{h}{2}<x<+\infty, \tag{3}$$

$$c\left(-\frac{h}{2},t\right)=c_0(1-\mathrm{e}^{-at}), \qquad D\left.\frac{\mathrm{d}c}{\mathrm{d}x}\right|_{x=h/2}=0, \tag{4}$$

$$\frac{1}{\nu}\int_{-h/2}^{h/2}\left(-\frac{\partial u_x}{\partial x}\right)\mathrm{d}x-\frac{w}{1-2\nu}\int_{-h/2}^{h/2}(c(x)-c_\mathrm{h})\,\mathrm{d}x=0,$$
$$\frac{1}{\nu}\int_{-h/2}^{h/2}\left(-\frac{\partial u_x}{\partial x}\right)x\,\mathrm{d}x-\frac{w}{1-2\nu}\int_{-h/2}^{h/2}(c(x)-c_h)x\,\mathrm{d}x=0, \tag{5}$$

where c_0 is the equilibrium concentration equal to the hydrogen solubility in the metal at the hydrogen pressure P, h the thickness of the plate. Given the initial and boundary conditions, Eqs. (1) and (2) describe the time dependence of the hydrogen distribution and displacement of the medium points. With the known hydrogen distribution in the specimen, we calculated the time dependence of displacement Δy for free end of the specimen.

Calculations showed that above mentioned reason of the Δy_{irr} existence works actually. It is graphically well shown in Fig. 2, in which one can see dependences of hydrogen concentration in a membrane subsurface layer on a copper covered side. It is possible to see (curve 1) that hydrogen concentration along the membrane width levels off quickly if Fick diffusion would work. However, an appearance of hydrogen elastic stresses slows down diffusion, and the growth of hydrogen concentration on a "far" side of the membrane is so greatly slowed down that it goes into some steady-stable state (curve 2). In other words, some thermo-baroelastic-diffusive equilibrium may take place being fixed as a residual shape-changing of the membrane (Δy_{irr}).

Experimental and theoretical time dependences of the deflection ($T = 150\,^\circ\mathrm{C}$, $P_{\mathrm{H}_2} = 9\times10^3$ Pa), observed upon a one-side saturation of the palladium plate with hydrogen, were compared. The results are shown in Fig. 3. On the one hand, it is seen that the shapes of the theoretical and experimental curves are absolutely identical. However, it is clearly seen that the continuum model predicts a considerably higher effect in comparison with the experimentally observed one. The causes of this phenomenon must be additionally studied theoretically and experimentally. At present, it can only be supposed [8] that the stronger theoretical effects reflect the nature of the assumed model, where the metal is considered as a uniform and isotropic continuum with no peculiarities in its structure; i.e., the model takes into account the only way of relaxation of hydrogen-induced elastic stresses, namely, by bending the plate when the hydrogen atoms diffuse through the plate thickness. In fact, the metal is characterized by atomic, dislocation, mosaic, grain and other types of its real structure.

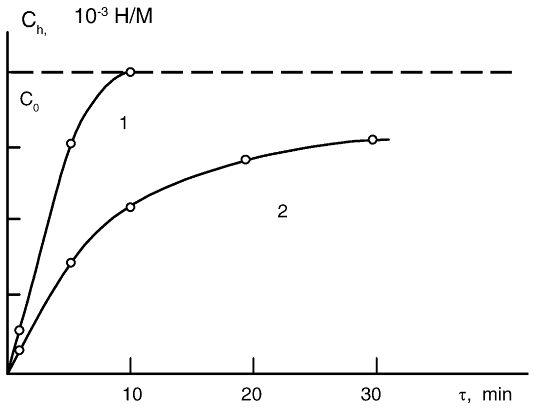

Fig. 2. Time dependence of the hydrogen concentration c_h in the near-surface regions of the impenetrable side of plate: (1) Fick's diffusion law; (2) hydrogen-elasticity model ($T = 100\,^\circ\mathrm{C}$, $P = 6\times10^3$ Pa).

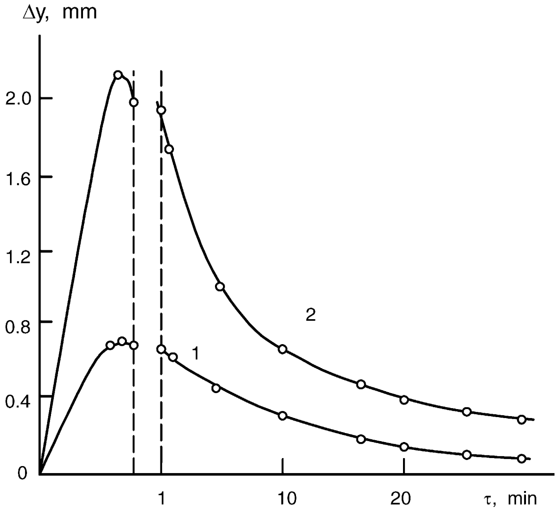

Fig. 3. Time dependence of the specimen deflection at $T = 150\,^\circ\mathrm{C}$ and $P = 9\times10^3$ Pa: (1) experimental curve; (2) curve calculated according to the hydrogen-elasticity model.

Therefore, it is clear that, in principle, for the hydrogen-induced elastic stresses that arise in a real metal plate, not only a macroscopic relaxation mechanism is possible (due to the diffusion of hydrogen atoms through the whole specimen) but also mechanisms of mesoscopic and microscopic scales can exists, e.g., due to the different elastic deformation and microshears of individual grains, by the microplastic deformation (generation of dislocations) under stresses that are lower than the microscopic yield stress, etc.

4. Conclusion

The experiments performed showed that upon one-side hydrogen saturation at different pressures and temperatures, the palladium plate changes its shape in a regular manner.

During the complete saturation–degassing cycle, the deformation can be considered reversible to a large extent. In the first stage of the hydrogen saturation–degassing cycle, the deformation can arbitrarily be divided into two components: reversible and irreversible. Thus, the contributions of the reversible and residual components to the total deformation change fundamentally. At 150 °C with increase of hydrogen pressure the total form changing and its reversible component grow. Irreversible one practically does not change. On the contrary, at 100 °C, reversible component behaves conservatively. With the increase of hydrogen pressure a total form changing and irreversible component grow.

The deformation of a palladium plate upon its one-side saturation with hydrogen (dependences on the time, temperature, and "hydrogen impact" pressure for the α solid solutions of hydrogen in metals) is sufficiently well described by hydrogen-elasticity model based on a set of nonlinear differential equations that describe the hydrogen elasticity on the whole as a general metallophysical phenomenon. One of the causes of the observed residual deformation of a palladium plate upon its single-side saturation with hydrogen is a retardation of hydrogen diffusion by hydrogen-induced classic stresses, which hinders concentration equalization over the plate thickness for reasonable experimental times.

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