334 *Int. J. Nuclear Hydrogen Production and Application, Vol. 1, No. 4, 2008*

The mathematical modelling of the hydroelastic effect of slowing down of the diffusion processes in metal-hydrogen systems

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Abstract: Computations were carried out involving the lifetime of macroscopic ball-shaped Hydrogen Concentration (HC) inhomogeneities in palladium. It was shown that hydrogen-elastic stresses slow down the solubility of HC inhomogeneities. The influence of hydrogen-elastic stresses increases considerably as inhomogeneity dimensions increase.

Keywords: metal-hydrogen systems; hydrogen diffusion; hydrogen-elastic effects.

Reference to this paper should be made as follows: Glukhova, Zh.L., Golstov, V.A., Schegoleva, T.A., Lyubimenko, E.N. and Kotelva, R.V. (2008) 'The mathematical modelling of the hydroelastic effect of slowing down of the diffusion processes in metal-hydrogen systems', *Int. J. Nuclear Hydrogen Production and Application*, Vol. 1, No. 4, pp.334–342.

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1 Introduction

Fick's diffusion becoming slower by Hydrogen Concentration (HC) stresses is one of the most widespread hydrogen-elastic effects (Goltsov, 2001). This effect is a physical reason for a considerable slowing down of many processes connected with diffusion phenomena in Metal-Hydrogen (MeH) systems. In the works of Goltsov *et al.* (1997; 2001), it was shown for the first time that when considering diffusion phenomena in MeH systems, the role and a possible importance of hydrogen-elastic effects should not be neglected (without a special analysis). In this paper, it was of interest to continue developing the physical and mathematical aspects of the diffusion-elastic model (Goltsov *et al.*, 1997; 2001) on the basis of the equations of isothermal hydrogen elasticity (Goltsov *et al.*, 2003), keeping in mind the importance of MeH systems, in particular, a possibility for ascending diffusion. The model developed in the works of Goltsov *et al.* (1997; 2001) does not provide for such a physical possibility.

2 Results and discussion

The nature of the hydrogen elasticity phenomenon is as follows. Interstitial hydrogen atoms expand a crystal lattice. Hence, any hydrogen inhomogeneities and any HC gradients cause the appearance of corresponding HC stresses. Fields of HC stresses influence hydrogen diffusion and cause a rearrangement of HC fields and so on. It is evident that any changing in HC fields and HC stress fields are interrelated. The hydrogen elasticity phenomenon takes place in metals, compounds and other materials when hydrogen stresses do not overcome a material limit of proportionality.

The hydrogen elasticity phenomenon comprises hydrogen elastic mechanical effects (a macroscopic reversible form-changing effect, the Gorsky effect, a reversible coherent swelling of a surface) and hydrogen elasticity diffusive effects (the slowdown of a hydrogen diffusive flow, an uphill hydrogen diffusive slow, the Lewis effect, thermo-baro-elastic-diffusive equilibrium effect).

From the viewpoint of mathematics, the phenomenon of hydrogen elasticity is described by the system of the related differential equations, one of which is the equation of diffusion with the term that includes an influence of the field of elastic stresses. The other equation is the equation of movement, which covers a concentration field influence. These equations are supplemented with the equations of state connecting the components of the stress tensor σ_{ij} and deformation tensor ε_{ij} and with the equations of bonding between the deformation tensor and displacement vector u_i components. Below, two of the approaches that we used for a mathematical description of the hydrogen elasticity phenomenon are presented.

2.1 The first approach

At the first stage of investigating the hydrogen elasticity phenomenon, we used the equations of hydrogen elasticity that were written by analogy with the equations of thermal elasticity (Goltsov *et al*., 1997). The equations describing the space and time variations of the deformation field and HC one are as follows:

$$\mu\nabla^2\vec{u} + (\lambda+\mu)grad \cdot div\vec{u} - (3\lambda+2\mu)\alpha_H \cdot grad\ c - \rho\frac{\partial^2\vec{u}}{\partial t^2} = 0, \tag{1}$$

$$\nabla^2 c - \frac{1}{D}\frac{\partial c}{\partial t} - \frac{(3\lambda+2\mu)\cdot\alpha_H B_c c}{D} div\dot{\vec{u}} - 0, \tag{2}$$

where:

c = a relative atomic HC similar to temperature T in thermo-elasticity
u = a displacement vector
ρ = material density
λ and μ = Lame coefficients
α_H = a linear hydrogen concentration expansion coefficient that is similar to a linear thermal expansion one
$B_c = \dfrac{dc}{dp}$
p = hydrogen gas pressure
D = a hydrogen diffusion coefficient corresponding to a temperature conductance coefficient in thermo-elasticity.

Equations (1) and (2) are bound, owing to term $(3\lambda + 2\mu)\alpha_H \cdot grad\, c$ in Equation (1) and term $\dfrac{(3\lambda+2\mu)\cdot\alpha_H B_c c}{D} div\dot{\vec{u}}$ in Equation (2). They describe the deformation of a solid body resulting from no stationary mechanical and HC effects as well as a reverse effect – a change in the concentration field of hydrogen in a solid body due to its deformation.

Then, using the relations between displacements and deformations and Hooke's law (known in elasticity theory), one may proceed to stresses. Thus, Equations (1) and (2) describe a mutual relation and mutual influence of hydrogen distribution evolution and hydrogen-elastic stresses evolution in a solid body.

2.2 The second approach

Then, on the basis of classical elasticity theory, thermodynamics of non-equilibrium processes and empiric regularities, the equations of isothermal hydrogen elasticity were written (Goltsov *et al.*, 2003):

- a generalised temporal equation of time-dependent diffusive transport of hydrogen:

$$\frac{\partial c}{\partial t} = \operatorname{div}\left[D^{*} \operatorname{grad} c - \frac{D^{*} c\, A\alpha_{H}}{\rho RT} \operatorname{grad} \sigma_{kk} \right], \tag{3}$$

- the equations of motion:

$$\frac{\partial \sigma_{ij}}{\partial x_{j}} = \rho \ddot{u}_{i}, \tag{4}$$

- the equations of state:

$$\varepsilon_{ij} = \frac{1+v}{E}\sigma_{ij} + \left[\alpha_{T}(T-T_{0}) + \alpha_{H} c - \frac{v}{E}\sigma_{kk} \right]\delta_{ij}, \tag{5}$$

- the equations that relate the components of the deformation tensor ε_{ij} to the components of the vector of motion u_i:

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_{i}}{\partial x_{j}} + \frac{\partial u_{j}}{\partial x_{i}} \right). \tag{6}$$

The written set of equations of isothermal hydrogen elasticity describes (at T = const.) the interrelated evolution of elastic fields of the matrix and the fields of HCs.

We matched these two approaches of describing the hydrogen elasticity phenomenon when solving the problem of dissolution of HC inhomogeneities in palladium, taking into account the arising stresses. In Goltsov *et al.* (1997), such a task was solved on the base of the hydrogen elasticity Equations (1) and (2) written down in analogy with the thermo-elasticity equations. In this paper, the mathematical model describing the behaviour of HC inhomogeneities is built on the base of the system of equations of isothermal hydrogen elasticity (Equations 3 to 6).

The physical essence of the problem under consideration is as follows. A macroscopic sphere is taken out of an infinite medium; the sphere is saturated with hydrogen to some concentration c_O. Then, this sphere is inserted in an earlier formed cavity. As the cavity radius is less than the radius of a newborn sphere, then deformations and stress appear both in the sphere and in the medium around it. What is especially important is that in every case, the sphere's initial sizes and the values of HC were to be chosen in such a way that the appearing initial stresses did not exceed a metal elastic limit.

When considering the behaviour of HC inhomogeneities in the form of a sphere and keeping in mind the appearing hydrogen-elastic stresses, we obtain a case of a polar-symmetric stressed state. Here, only a radial motion u_r is different from zero. All the components of deformations and motions excluding $\varepsilon_{rr}=\frac{\partial u_r}{\partial r}$; $\varepsilon_{\theta\theta}=\varepsilon_{\varphi\varphi}=\frac{u_r}{r}$ и σ_{rr}, $\sigma_{\theta\theta}=\sigma_{\varphi\varphi}$ will be equal to zero (in the spherical coordinate system).

As the relaxation time for mechanical movements is negligibly small in comparison with the one for diffusion, an inertial member $\rho\ddot{u}$ in the equation of motion is believed to be equal to zero and we go over to the equilibrium equation. With the stresses in the equilibrium equation and diffusion equation being expressed in terms of deformations and the deformations being expressed in terms of displacements, let us go over to the corresponding equations in the displacements. In the spherical coordinate system, they have the following form:

$$\frac{\partial c}{\partial t}=D\frac{\partial^2 c}{\partial r^2}+\frac{2D}{r}\frac{\partial c}{\partial r}+Mc\frac{\partial^3 u}{\partial r^3}+\frac{4M}{r}c\frac{\partial^2 u}{\partial r^2}+N\frac{\partial^2 c}{\partial r^2}+\frac{2N}{r}\frac{\partial c}{\partial r}, \tag{7}$$

$$L\frac{\partial^2 u}{\partial r^2}+\frac{2L}{r}\frac{\partial u}{\partial r}-\frac{2L}{r^2}u+F\frac{\partial c}{\partial r}=0, \tag{8}$$

where $L = A + B$, $M = -G(A + 3B)$, $N = -3GF$;

$$A=\frac{E}{1+v},\ B=\frac{vE}{(1+v)(1-2v)},\ F=-\frac{E}{1-2v}\alpha_H,\ G=\frac{DK}{T},$$

c = HC
r = a radial coordinate
t = time
D = hydrogen diffusion coefficient
T = temperature
$K = A_M\alpha_H/\rho R$ = a constant
A_M = a metal atomic mass (Pd)
α_H = a metal linear expansion coefficient at hydrogen dissolving
ρ = a metal density
R = the absolute gas constant
σ_{rr}, $\sigma_{\theta\theta}$ and $\sigma_{\varphi\varphi}$ = stress tensor components.

Keeping in mind that an infinite medium is under consideration, the boundary conditions are written in this way:

$$c(\infty,t)=0 \tag{9}$$

$$u_r(\infty,t)=0. \tag{10}$$

The initial conditions for HCs are given in the following form:

$$c(r,0)=\begin{cases} c_o \text{ для } 0\le r\ge R \\ 0 \text{ для } r\ge R. \end{cases} \tag{11}$$

The analysis of Equations (7) and (8) shows that distribution $u_r(r,0)$ can be obtained from Equation (8) by the given initial conditions (Equation 11) for HCs.

Differential Equations (7) and (8) under the boundary and the initial conditions (Equations 9 to 11) make up a closed system of equations which are a mathematical model of a temporal behaviour of sphere-shaped concentration inhomogeneities of hydrogen in an infinite elastic medium (for example, in a metal whose elastic properties are characterised by Young's modulus E and Poisson's ratio ν).

A mathematical modelling was concretely defined, as in Goltsov *et al.* (1997), for the system palladium-hydrogen at the following values of constants: $E = 1.15 \times 10^{11}\Pi\alpha$; $\nu = 0.3$; $\alpha_H = 0.063$. The temperature was measured in the range of 300–700 K. The radius of inhomogeneities varied from 1 to 5 mm. The initial HCs were changed from 0.001 to the maximum values when the initial stress did not exceed $\sigma_{0.2}$ ($\sigma_{0.2} = 56$ MPa). The radius of inhomogeneities increases and, as a natural result, a permissible HC that causes stresses larger than $\sigma_{0.2}$ of palladium decreases. To compare numerical computations, an initial HC in the inhomogeneities in all cases was taken equal to 0.006.

The system of Equations (7) and (8) with the given initial and boundary conditions was solved by numerical methods with the use of specialised software. The programme makes it possible to obtain dependences $c(r)$, $\sigma_{rr}(r)$, $\sigma_{\theta\theta}(r)$, $\varepsilon_{rr}(r)$, $\varepsilon_{\theta\theta}(r)$ and $u_r(r)$ and display them in the given periods of time.

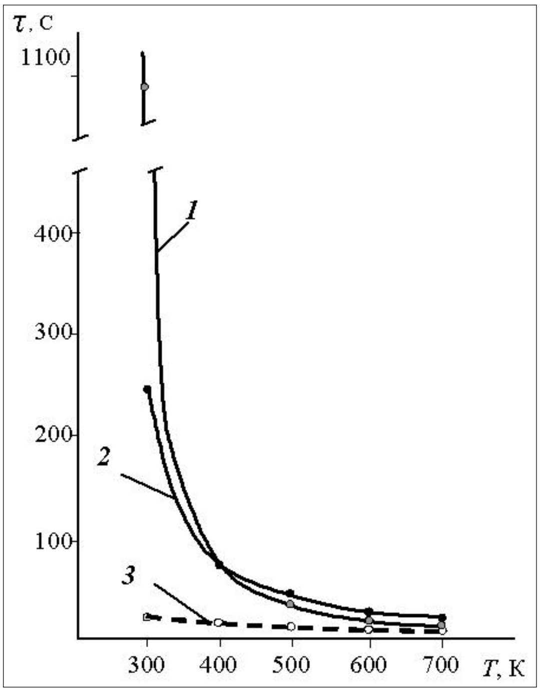
The main results of the 'computer experimentation' on the basis of the developed mathematical model of the diffusion-elastic behaviour of a sphere-shaped concentration inhomogeneity of hydrogen in palladium are as follows.

A temporal picture of the evolution of concentration curves and a corresponding evolution of the field of stresses, deformations and displacements have been obtained. Comparison of all the concentration curves was done by the parameter τ that characterised the lifetime of inhomogeneities, this lifetime being taken as the time of a double decrease of HC in an inhomogeneity centre. The corresponding quantitative characteristics of the model 'lifetime' were generalised in the form of dependences of an inhomogeneity lifetime τ on temperature T and their initial sizes R_o.

The results of the computer investigations are summarised in Figures 1 and 2. In Figure 1, the data from Goltsov *et al.* (1997) are dotted to make a comparison. Curve 2 gives the temperature dependence of a concentration inhomogeneity lifetime in the case where hydrogen-elastic stresses do not work and an inhomogeneity resorption is defined only by Fick's diffusion. Curve 3 presents the temperature dependence of an inhomogeneity lifetime in the case where operating hydrogen-elastic stresses are modelled by analogy with temperature stresses (Goltsov *et al.*, 1997).

As can be seen in Figure 1, both models of the hydrogen elasticity phenomenon (compare Curves 1 and 2 and Curve 3) give qualitatively close results: at every temperature, the resorption of an HC inhomogeneity becomes much slower when HC stresses (Curves 1 and 2) are in force in comparison with the model when a diffusion mechanism of resorption takes place according to Fick's law. It is noteworthy that as the temperature decreases, the slowdown becomes more apparent. For example, at 300 K, the time of the only diffusion resorption of an inhomogeneity is 23 sec (Curve 3) and in the case of a hydrogen-elastic model, $\tau = 18$ sec (Curve 1). The diffusion process of an inhomogeneity resorption becomes slower by a factor of 47.

Figure 1 Temperature dependence of the lifetime of a concentration inhomogeneity of a 1 mm radius with the initial concentration $c_0 = 0.006$



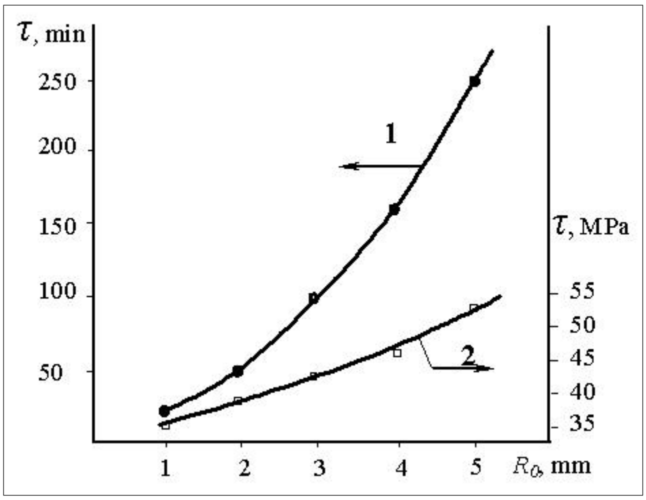
Notes: (1) an elastic-diffusion regime (the isothermal hydrogen elasticity equations are used); (2) an elastic-diffusion regime (Goltsov *et al.*, 1997); (3) the diffusion regime only.

Now, let us analyse the operation of the two hydrogen-elastic models (Curves 1 and 2). First of all, we should emphasise that both models give qualitatively close results. They mean one and the same tendency of hydrogen-elastic stress influencing the diffusion processes in metal-hydrogen systems. What is more, Curves 1 and 2 show a similar temperature dependence of hydrogen-elastic stress influencing the diffusion processes in metal-hydrogen systems.

The computer calculations of a new model showed that as inhomogeneity sizes increase and the stresses appearing therewith increase too, the slowdown effect becomes much more stronger. At the same conditions, inhomogeneities that are 5 mm in diameter have τ increased by a factor of more than 10 (in comparison with the data for inhomogeneities with $R_0 = 1$ mm). It is clearly seen in Figure 2 (Curve 1).

In this very picture, a dependence of the maximum value of stresses (of all components) on an inhomogeneity radius (Curve 2) is shown. In Figure 2, one can see a determining importance of hydrogen-elastic stresses and their value for the diffusion processes in metal-hydrogen systems. In this respect, we should once again emphasise the most important feature of metal-hydrogen systems: their diffusion behaviour cannot be adequately understood only on the base of Fick's law. Let us explain the thought in this way.

Figure 2 Dependence of a concentration inhomogeneity lifetime (1) and maximum stresses (2) on the inhomogeneity radius ($T = 300$ K, $c_o = 0.006$)



The calculations show that in the diffusion regime (Figure 1, Curve 3), only the temperature has a significant influence on the dissolving rate of inhomogeneities. As the hydrogen diffusion coefficient decreases with the decreasing temperature, then both the diffusion rate and inhomogeneity lifetime decrease. An inhomogeneity radius changing from 1 to 5 mm does not practically tell on the lifetime τ. Then, as in the case of stress influence on the diffusion process, the changes of a sphere radius from 1 to 5 mm cause maximum stresses to increase by 44%. This results in the observed slowdown of the diffusion dissolving of the inhomogeneity: τ changes from 18 min for $R_o = 1$ mm to 250 min for $R_o = 5$ mm (Figure 2, Curve 1).

We emphasise that at temperatures below 400 K, according to the model based on the isothermal hydrogen elasticity equations, a stronger effect of the slowdown is observed. We think that this can be explained in this way. The isothermal hydrogen elasticity equations, as the basis of a new behavioural model of concentration inhomogeneities presented in this paper, imply a possibility of ascending diffusion. This fundamental feature of MeH systems is not taken into account in the equations of hydrogen elasticity written by analogy with the equations of thermal elasticity. This implies that a new hydrogen-elastic model based on the isothermal hydrogen elasticity equations more fully reflects the peculiarities of the phenomenon of hydrogen elasticity and is adequate to the diffusion-cooperative nature of metal-hydrogen systems.

3 Conclusion

This paper summarises the current knowledge of the phenomenon of hydrogen elasticity in metal-hydrogen systems. The systems of the connected nonlinear differential equations are given, which are the basis of the mathematical modelling and computer calculations of specific developments of the hydrogen elasticity phenomenon.

On the basis of the system of the isothermal hydrogen elasticity equations, a mathematical model describing the behaviour of HC inhomogeneities in palladium and the basic regularities of their elastic-diffusion dissolution was developed. An analysis of the computer calculations showed that hydrogen-elastic stresses greatly slow down diffusion processes and the inhomogeneity lifetime essentially increases. The largest effect is observed at room temperatures.

Comparison of the computer results obtained in this work and the ones obtained before (Goltsov *et al.*, 1997) allowed us to conclude that the new hydrogen-elastic model based on the isothermal hydrogen elasticity equations more fully reflects the diffusion-cooperative nature of metal-hydrogen systems.

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